University of Alberta

Seven-Membered Ring Compounds from [3+2+2] and [5+2] Cobalt-Mediated Cycloadditions

by

Ross Davidson Witherell ©

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
Fall 2007

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-33093-7
Our file Notre référence
ISBN: 978-0-494-33093-7

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

For My Parents

Abstract

A number of developments in cobalt-mediated cycloadditions yielding seven-membered rings are presented in which metal-templated ligands are incorporated into carbocycles upon reaction with alkynes. In one such process, allyl ligands bearing tethered latent nucleophiles are incorporated via a [3+2+2] process into Cp*Co(III) η^5-cycloheptadienyl complexes. The diastereoselective conversion of these complexes into *bicyclic* organic fragments via intramolecular nucleophilic attack is described.

In addition, a new method for the efficient decomplexation of conjugated dienes from Cp*Co(I) templates is described, in which both the organic fragment and the metal template may be recovered in a useful form.

As part of an investigation into the potential utility of the [3+2+2] cycloaddition for the synthesis of bicyclic organic compounds exhibiting the unusual "inside-outside" stereochemistry, mechanistic insight has been gained with respect to the addition of nucleophiles to Cp*Co(III) η^5-cycloheptadienyl ligands.

The synthesis of several novel Cp*Co(III) siloxyallyl complexes is described, as well as the unprecedented incorporation of an oxygen-bearing allyl ligand into a cycloheptadienone product via the [3+2+2] cycloaddition.

A novel [5+2] cycloaddition reaction is described in which alkynes are incorporated into a Co(III)-templated η^5-pentadienyl ligand to generate seven-membered rings. In this manner, complexes exhibiting an η^3,η^2-hapticity are accessed; these complexes represent the first examples of such a hapticity in non-bridged seven-membered ring compounds. The efficient conversion of these compounds into more

familiar Co(III) η^5-cycloheptadienyl complexes is described, and the mechanism by which the [5+2] cycloaddition proceeds is explored.

Table of Contents

Chapter 1 – Recent Developments in Metal-Mediated Cycloadditions for the Synthesis of Seven-Membered Carbocycles 1

Part A: Cycloadditions and Cyclizations in Organic Synthesis 1

Part B: Recent Developments in Seven-Membered Carbocycle Cyclizations 3

Part C: Recent Developments in [5+2] Cycloaddition Methodology 4

Part D: Recent Developments in [4+3] Cycloaddition Methodology 12

Part E: Recent Developments in Higher-Order Cycloaddition Methodology 15

Chapter 2 – Bicyclic Organic Molecules From a Cobalt-Mediated [3+2+2] Cycloaddition 21

Section 1: Introduction 21

Part A: Cobalt-Mediated [3+2+2] Allyl/Alkyne Cycloadditions 21

Part B: Nucleophilic Elaboration and Oxidative Decomplexation of Cycloheptadienyl Ligands 41

Part C: Incorporation of Pro-Nucleophilic Functionalities in [3+2+2] Cycloadditions 46

Section 2: Results and Discussion 51

Part D: Synthesis of Cp*Co(III) Allyl Halides Bearing Latent Nucleophiles 51

Part E: Synthesis of Bicyclic Organic Compounds via [3+2+2] Cycloaddition 60

Part F: Oxidative Decomplexation of Bicyclic Organic Products 70

Part G: Cobalt Mediated [3+2+2] Cycloadditions as a Route to "Inside-Outside" Stereochemistry 74

Part H: Summary and Outlook. 93

Chapter 3 – Oxygen-Bearing Seven-Membered Carbocycles 95

Section 1: Introduction 95

Part A: 1-Hydroxyallyl and 1-Silyloxyallyl Chemistry 95

Section 2: Results and Discussion 102

Part B: Synthesis and Characterization of Cp*Co(III) Hydroxyallyl Complexes 102

Part C: Synthesis and Characterization of Cp*Co(III) Silyloxyallyl Complexes 114

Part D: Summary and Outlook 132

Chapter 4 – Seven-Membered Carbocycles From a Cobalt-Mediated [5+2] Pentadienyl/Alkyne Cycloaddition 139

Section 1: Introduction 139

Part A: Pentadienyl Ligands in Cycloaddition Chemistry 139

Part B: Cobalt(III) Pentadienyl Complexes as a Possible Intermediate in a [5+2] Ring-Expansion Process Involving a Carbon-Carbon Bond Activation 155

Part C: 1,2,4,5,6-η^2,η^3-Cycloheptadienyl Complexes in Organometallic Chemistry 171

Section 2: Results and Discussion 179

Part D: Synthesis of Cp*Co(III) Pentadienyl Complexes 179

Part E: Reactivity of Cp*Co(III) Pentadienyl Complexes with Alkynes – An Unprecedented Thermal [5+2] Cycloaddition Reaction. 198

Part F: Summary and Future Work 233

Chapter 5 – Experimental 238

Part A: General Experimental 238

Part B: Chapter 2 Experimental Section 241

Part C: Chapter 3 Experimental Section 280

Part D: Chapter 4 Experimental Section 291

Notes and References 325

List of Tables

Table 3.1: ^{1}H NMR Data for Compound **245** 105

Table 3.2: ^{1}H NMR Data for Compound **246** 107

Table 3.3: ^{1}H NMR Data for Cp*Co(III) Silyloxyallyl Halides **261**, **262**, and **263** 118

Table 3.4: ^{13}C NMR Data for Cp*Co(III) Silyloxyallyl Halides **261**, **262**, and **263** 119

Table 3.5: Carbonyl Stretching Frequencies from Several Cycloheptadienones 124

Table 3.6: Summarized ^{1}H Data for **286** 130

Table 4.1: Comparative ^{13}C NMR Spectroscopic Data for Cp*Co(III) Pentadienyl Hexafluorophosphate Salts in CH_2Cl_2-d_2 189

Table 4.2: Comparative ^{1}H NMR Spectroscopic Data for Cp*Co(III) Pentadienyl Hexafluorophosphate Salts in CH_2Cl_2-d_2 190

Table 4.3: Selected ^{1}H NMR Spectroscopic Data for Cp*Co(III) η^2,η^3-Cycloheptadienyl Hexafluorophosphate Salts **456** and **477** in CH_2Cl_2-d_2 210

List of Figures

Figure 1.1: Examples of Natural Products Containing Seven-Membered Rings 1

Figure 2.1: ORTEP for Complex **137** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0404 59

Figure 2.2: ORTEP for Complex **173** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0312 68

Figure 2.3: ORTEP for Complex **189** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0344 77

Figure 2.4: ORTEP for Complex **189** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0344 84

Figure 2.5: ORTEP for Complex **204** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0406 86

Figure 2.6: ORTEP for Complex **205** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0325 88

Figure 3.1: ^{1}H NMR Spectrum of **245** Formed *In Situ* in Acetonitrile-d_3 (solvent: δ 1.95) 106

Figure 3.2: ^{1}H NMR Spectrum of **245** After Acetylene Stream 107

Figure 3.3: ^{1}H NMR Spectrum of **246** Formed *In Situ* in Acetone-d_6 (solvent: δ 2.04) 108

Figure 3.4: ^{1}H NMR Spectrum of **246** After Acetylene Stream 108

Figure 3.5: ORTEP for Complex **247** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0304 110

Figure 3.6: ORTEP for Complex **262** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0327 117

Figure 3.7: ORTEP for Complex **267** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0337 123

Figure 3.8: ^{1}H NMR Spectrum of Crude **286** 131

Figure 4.1: Examples of the Various Binding Modes Available to the Pentadienyl Ligand 140

Figure 4.2: ORTEP for Complex **430** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0423 194

Figure 4.3: ORTEP for Complex **452** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0452 195

Figure 4.4: ORTEP for Complex **453** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0520 196

Figure 4.5: ORTEP for Complex **454** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0570 197

Figure 4.6: ORTEP for Complex **456** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0435 200

Figure 4.7: ORTEP for Complex **439** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0439 222

Figure 4.8: Four Possible [5+2] Cycloadducts from Complex **453** 232

List of Abbreviations

Å	Angstrom
app.	Apparent
Bn	Benzyl
br	Broad
COSY	Correlated Spectroscopy
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Cp'	η^5-methylcyclopentadienyl
d	Doublet
DGM	Davies-Green-Mingos Rules
DMAD	Dimethyl acetylenedicarboxylate
E	-CO_2Me
eq	Equivalents
Fc	Ferrocenyl
GCOSY	Gradient COSY
HMBC	Heteronuclear Multiple Bond Coherence
HMQC	Heteronuclear Multiple Quantum Coherence
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
IR	Infra-red
L	Ligand

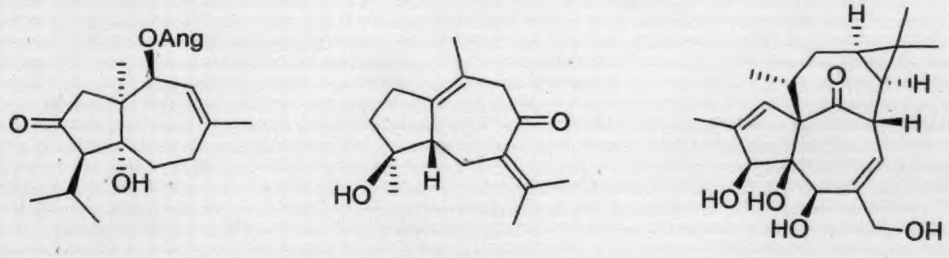
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal
Me	Methyl
MO	Molecular Orbital
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
OAc	Acetate
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	Trifluoromethanesulfonate (triflate)
Ph	Phenyl
Pr	Propyl
q	Quartet
R	Alkyl, Aryl, or Vinyl
s	Singlet
S	Solvent
t	Triplet
TFE	2,2,2-Trifluoroethanol
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TMS	Trimethylsilyl

Chapter 1 – Recent Developments in Metal-Mediated Cycloadditions for the Synthesis of Seven-Membered Carbocycles

Part A: Cycloadditions and Cyclizations in Organic Synthesis

The seven-membered carbocycle is a common feature of a large number of natural products; a number of diterpenoids[1-7] and sesquiterpenoids[8-14] of the guaiane, carotane, and daucane groups (Figure **1.1**) are some representative examples.

Figure 1.1: Examples of Natural Products Containing Seven-Membered Rings



a 3-oxodauc-8-ene neoprocurcumenol ingenol

Despite the abundance of seven-membered carbocycles in nature, the synthesis of these frameworks still presents a significant challenge to the organic chemist. Although a host of general methodology is available for the construction of five- and six-membered carbocycles, relatively few methods exist today for the preparation of the seven-membered ring, and those that do exist are most often limited to very specific substrates or substrate families. In order to best appreciate this dichotomy, it is helpful to recognize that any ring-forming process may be classified either as a cyclization, or as a cycloaddition.

A cyclization reaction is a reaction in which a single molecule closes in an intramolecular fashion by the formation of a bond between two atoms separated by one or more additional atoms. A cyclization reaction might simply involve the intramolecular reaction between two mutually reactive functional groups, without any metal catalysis or mediation; when this is the case, the number of intervening atoms between the two functional groups determines the size of ring. In large part, the difficulty in preparing seven-membered carbocycles by cyclization reactions lies in the higher enthalpic and entropic barriers associated with their formation relative to smaller ring sizes. Many intramolecular cyclization reactions that are successfully applied to five- and six-membered ring synthesis fail in larger rings because of competing intermolecular processes, often despite the reactions being performed under high dilution.

By contrast, a cycloaddition reaction generates a cyclic structure from two or more distinct molecules or molecular fragments. The intramolecular cycloaddition is distinguished from a cyclization reaction in that, in the former case, a new ring must be formed that does not incorporate the tether. The commonly employed notation used to categorize cycloaddition processes is one in which the number of carbons contributed by each component is summarized within square brackets. The cycloaddition of the 3-carbon oxyallyl fragment with the 4-carbon diene fragment, for example, is described as a [4+3] cycloaddition. It is important to recognize that this designation is not intended, in this context, to imply a concerted pathway; indeed, the vast majority of metal-mediated cycloaddition reactions proceed in a stepwise fashion. This occasionally makes the distinction between a cyclization and a cycloaddition reaction somewhat murky, as the final carbon-carbon bond forming (and ring closing) event in a *non-concerted* cycloaddition pathway might be viewed strictly as a cyclization event. Generally (and throughout the remainder of this discussion) a stepwise cycloaddition process is one in which the final carbon-carbon bond forming event proceeds from an intermediate which has a short lifetime, precluding its isolation under normal reaction conditions.

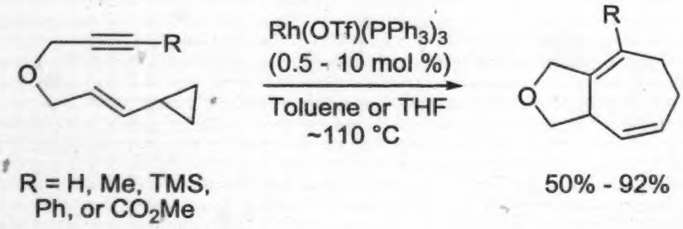
Methods that accomplish the formation of seven-membered rings are of great value to chemists and the development of general methods for these transformations represents an active and vital area of modern organic and organometallic chemistry. Although seven-membered carbocycle synthesis is still a difficult challenge, there now exist a small number of well established methodologies for this process. Many of them have been previously reviewed,[15,16] and Dr. Trevor Dzwiniel's Ph.D. dissertation[17] provides an excellent overview of much of the work done prior to 1999. As such, the following survey will place particular emphasis on technologies that have emerged since 1999, as well as on previously existing methodologies that have since seen significant further development.

Part B: Recent Developments in Seven-Membered Carbocycle Cyclizations

Although there is a relative paucity of successful general methods for the closing of seven-membered carbocycles, several are worthy of note. The catalytic ring-closing metathesis strategies developed in the last decade or so have occasionally been applied with success to seven membered ring formation. Palladium-based carbon-carbon bond forming methodologies, such as the intramolecular Heck reaction,[18-21] have also found some success. Sato and Mori[22-24] have reported the successful closure of the seven-membered ring by a Nickel-catalyzed cyclization of dienes with tethered carbonyl groups. More recently, Itoh[25,26] reported the rhodium-catalyzed cyclization of allenenes under a CO atmosphere to generate seven-membered rings, and Murakami[27] described a synthesis of seven-membered cyclic ketones via a rhodium-catalyzed arylative ring expansion process. Green has generated cobalt-coordinated fluorinated cycloheptynes by an intramolecular elecrophillic attack of a Nicholas-type cation on an olefin,[28] and a functionalized cobalt-coordinated cycloheptenyne via ring closing metathesis.[29] As part of a total synthesis of (-)-colchine, Schmalz has generated two seven-membered rings in a single rhodium-catalyzed cascade.[30]

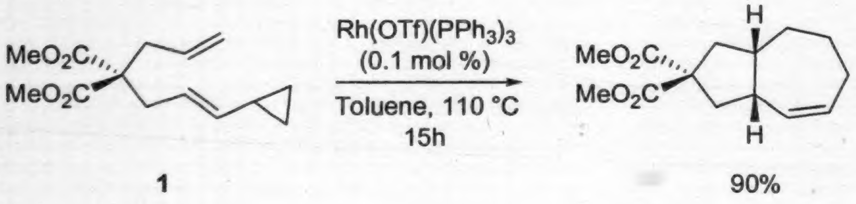
Part C: Recent Developments in [5+2] Cycloaddition Methodology

Historically, two-component cycloadditions to form seven-membered rings were primarily of the [4+3] type (*vide infra*), but some methods have recently emerged for [5+2] cycloaddition. The [5+2] *intramolecular* cycloaddition of vinylcyclopropanes to alkynes (Equation **1.1**) was first reported by Wender in 1995, and has been the subject of much research since.[31-47] The reaction is best catalyzed by the *in situ* generation of $Rh(OTf)(PPh_3)_3$ from Wilkinson's catalyst and silver triflate, although unmodified Wilkinson's catalyst could also be used in most cases. Catalyst loading was as low as 0.5 mole percent in some cases. Yields were generally high (~70 to ~90 %), and the reaction tolerated a fair degree of substrate functionalization. Terminal and internal alkynes were successfully incorporated into the product cycloheptadiene, and trisubstituted olefins were also viable substrates.


R
Rh(OTf)(PPh3)3
(0.5 - 10 mol %)
Toluene or THF
~110 °C
R
O
O
R = H, Me, TMS, Ph, or CO2Me
50% - 92%

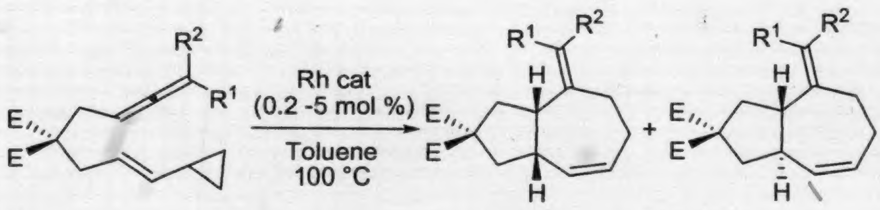
(Eq. 1.1)

More recently, Wender has successfully incorporated alkenes,[32] as well as allenes,[36] into the cycloaddition process. Equation **1.2** illustrates the successful reaction of the terminal monosubstituted olefin such as **1** with a vinylcyclopropane moiety; *disubstituted* terminal olefins may also be employed, in which case the reaction affords the *cis*-fused bicyclic product as the only diastereomer.


MeO2C
MeO2C
Rh(OTf)(PPh3)3
(0.1 mol %)
Toluene, 110 °C
15h
H
MeO2C
MeO2C
H
1
90%

(Eq. 1.2)

Mono-, di-, and trisubstituted allenes were also competent substrates for Wender's [5+2] cycloaddition, generating 7,5 fused bicyclic products bearing exocyclic olefins. The choice of catalyst was crucial in controlling the stereoselectivity of the cyclization: under otherwise identical reactions, $Rh(OTf)(PPh_3)_3$-catalyzed reactions gave poor diastereoselectivity for the *cis*-fused product whereas the alternative $[Rh(CO)_2Cl]_2$ catalyst[33] resulted in a better than 10 to 1 product ratio in favor of the *cis* isomer **2** (Equation **1.3**).

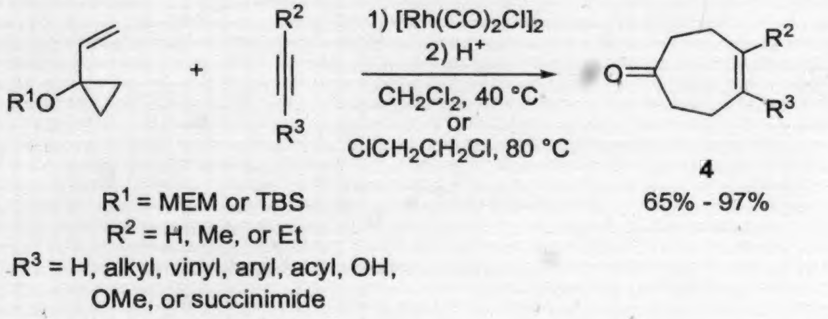


2 **3**

(Eq. 1.3)

Rh cat = $RhCl(PPh_3)_3$, $Rh(OTf)(PPh_3)_3$, or $[Rh(CO)_2Cl]_2$
E = CO_2Me
R^1 = H, Me, or *t*-Bu
R^2 = H or Me

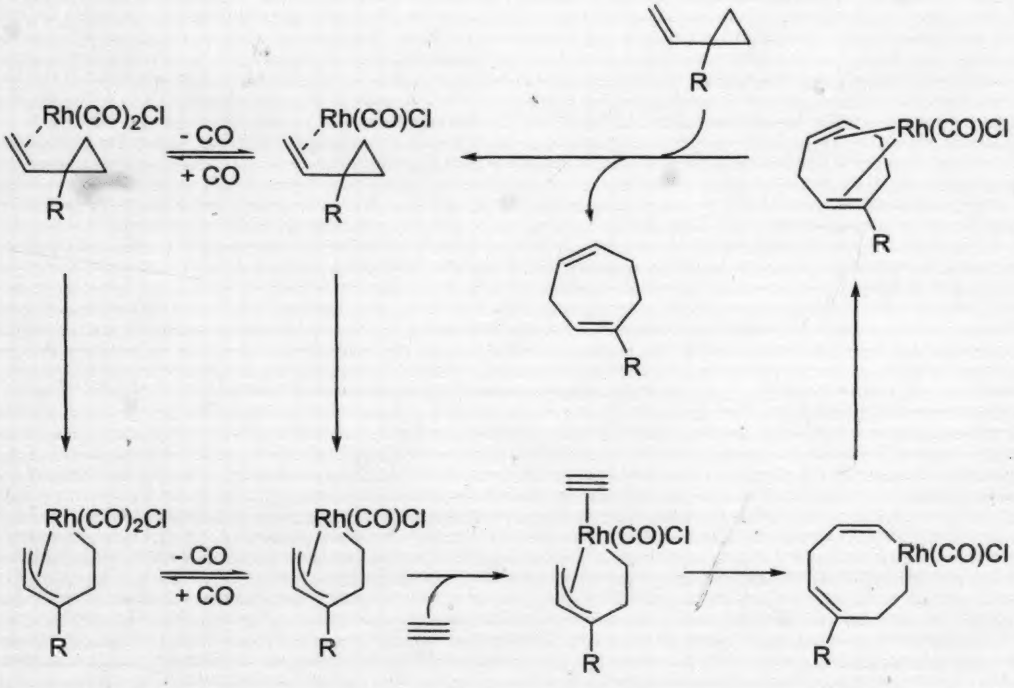
Whereas the previous examples were limited in scope to intramolecular reactions of substrates bearing alkynes, olefins, or allenes tethered to a vinylcyclopropane fragment, Wender has also extended this technology to mediate *intermolecular* reactions in which the 5-carbon vinylcyclopropane unit must bear a substituent at the 1-position of the cyclopropane component (Equation **1.4**). In the first examples, a tributylsiloxy[35] group was installed in this position; in later examples, methoxyethoxy[40] groups were incorporated. In either case, cycloheptenones **4** were isolated in good yields (65 to 97%) from a range of alkynes. Even more recently,[41] simple alkyl groups have been shown to be sufficient substituents for the promotion of the intermolecular reaction.


R¹O
+
R²
R³
1) [Rh(CO)₂Cl]₂
2) H⁺
CH₂Cl₂, 40 °C
or
ClCH₂CH₂Cl, 80 °C
O
R²
R³
4
65% - 97%
R¹ = MEM or TBS
R² = H, Me, or Et
R³ = H, alkyl, vinyl, aryl, acyl, OH,
OMe, or succinimide

(Eq. 1.4)

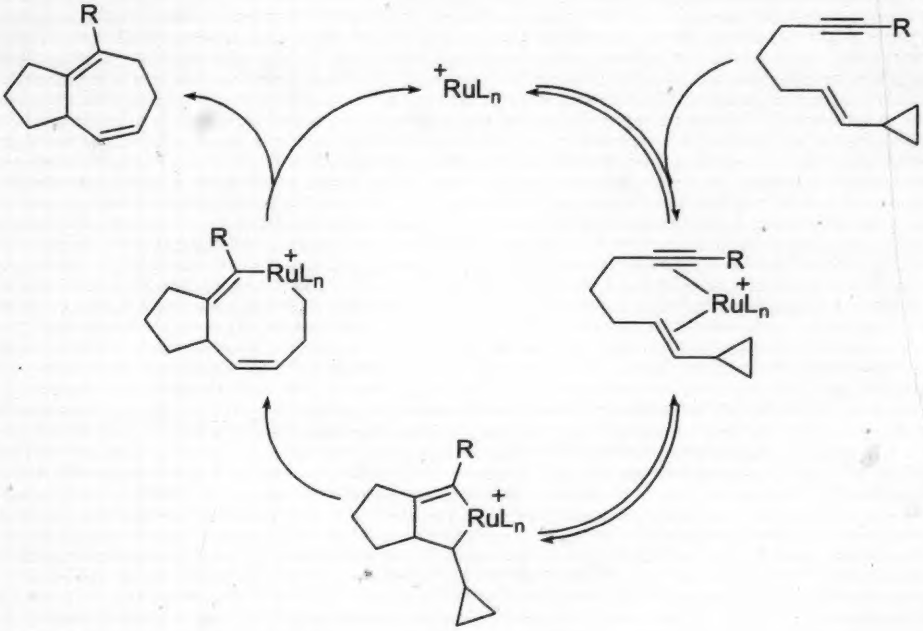
The mechanism of the [5+2] cycloaddition has been investigated by DFT calculations,[46] and the most likely pathway appears to be one in which the carbon-carbon bond of the cyclopropyl fragment is activated prior to alkyne coordination (Scheme **1.1**).

Scheme 1.1


R
Rh(CO)₂Cl
- CO
+ CO
Rh(CO)Cl
R
R
Rh(CO)Cl
R
R
Rh(CO)₂Cl
R
- CO
+ CO
Rh(CO)Cl
R
Rh(CO)Cl
R
Rh(CO)Cl
R

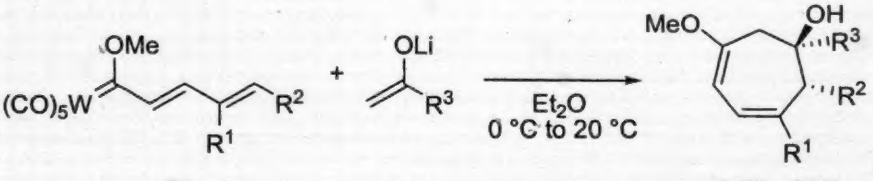
Trost[48-52] has also investigated the analogous [5+2] reaction catalyzed by the cationic ruthenium species, $CpRu(CH_3CN)_3PF_6$. In general, Trost observes the same general reactivity as Wender but Trost favors a mechanism which, at least in the ruthenium-catalyzed cases, invokes the alkyne-olefin coupling step before the cyclopropane carbon-carbon bond activation (Scheme **1.2**). It is noteworthy that the rhodium catalysts employed by Wender remain neutral throughout the process, whereas Trost's ruthenium catalysts are cationic; it is certainly possible that the order of mechanistic events (alkyne coupling and cyclopropane activation) are in fact different in either example, although no evidence for this has been reported.

Scheme 1.2



Although the systems disclosed by Wender and Trost are proficient in seven-membered ring production, one limitation of these (and other) systems is that a significant investment must be made in the synthesis of the substrates: tethered vinylcyclopropanes are strained ring intermediates requiring several synthetic steps.

Barluenga[53] has reported a formal [5+2] carbocyclization reaction between methyl ketone lithium enolates and doubly unsaturated methoxycarbene complexes of chromium and tungsten. In general, yields are better when tungsten pentacarbonyl complexes **5** are employed, and can range from 34% to as high as 86%, depending on the nature of the enolate and the carbene (Equation **1.5**).



34% - 86%
after acidic work-up

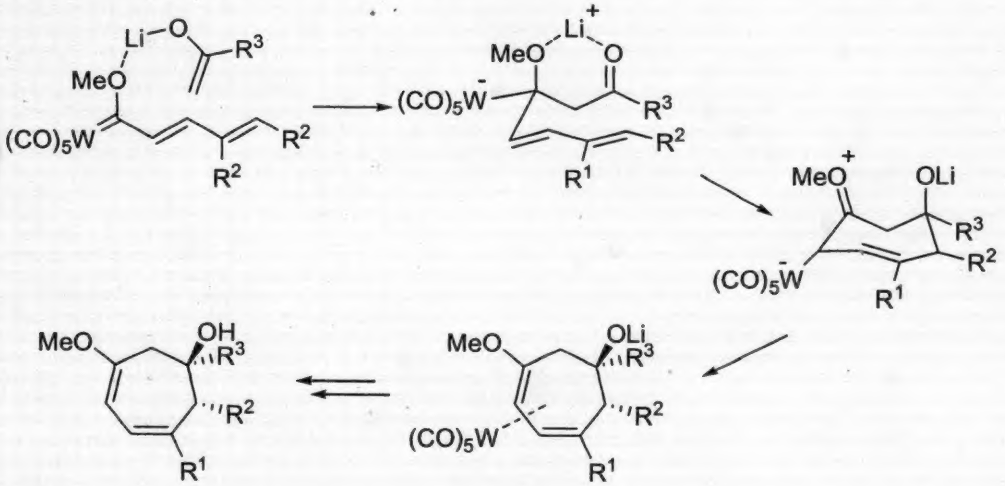
(Eq. 1.5)

R^1 = H, alkyl, or Cl
R^2 = Ph, 2-furyl, or alkyl
R^3 = aryl, 2-furyl, vinyl, or alkynyl

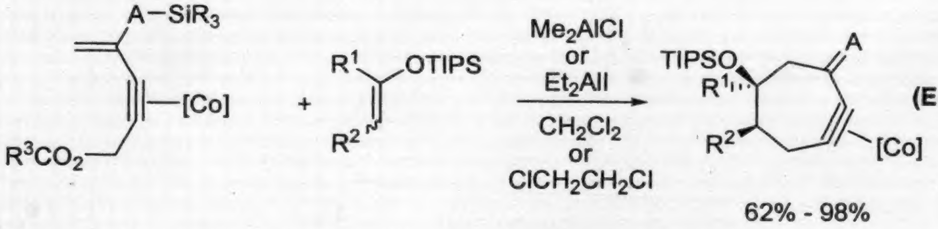
Barluenga proposes that this reaction, which is stoichiometric with respect to the metal, proceeds via a nucleophilic attack of the enolate on the carbene carbon, followed by a 1,2-migration of the metal fragment and concomitant cyclization to the seven-membered ring (Scheme **1.3**).

Tanino[54,55] has described a cobalt-mediated [5+2] cycloaddition coupling of silyl enol ethers **6** with 5-carbon Nicholas-type substrates **7** to generate cobalt-stabilized

Scheme 1.3


Li–O
R3
MeO
(CO)5W
R2
R2
MeO
Li+
O
(CO)5W−
R3
R2
R1
MeO+
OLi
R3
R2
(CO)5W−
R1
MeO
OH
R3
R2
R1
MeO
OLi
R3
R2
(CO)5W
R1

cycloheptyne adducts **8** bearing exocyclic double bonds (Equation **1.6**). A number of silyl enol ethers were surveyed and yields ranged from 62% to 98%. The reaction proceeds with reasonable diastereoselectivity. Regardless of the stereochemical configuration of the silyl enol ether, only a single diastereomer was obtained in most cases; in all cases the major diastereomer comprised better than 80% of the whole.


A–SiR3
[Co]
R3CO2
+
R1
OTIPS
R2
Me2AlCl
or
Et2AlI
CH2Cl2
or
ClCH2CH2Cl
TIPSO
R1
R2
A
[Co]
62% - 98%

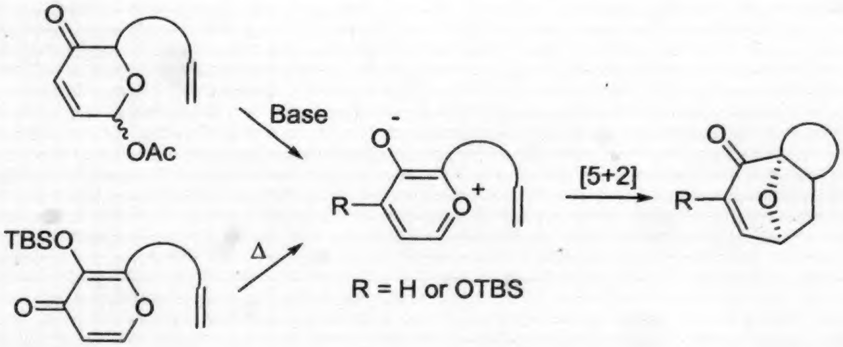
(Eq. 1.6)

7 **6** **8**

$[Co] = Co_2(CO)_6$
$A = CH_2$ or O
R^1 = H, [illegible] or Ph
R^2 = H, [illegible] Ph

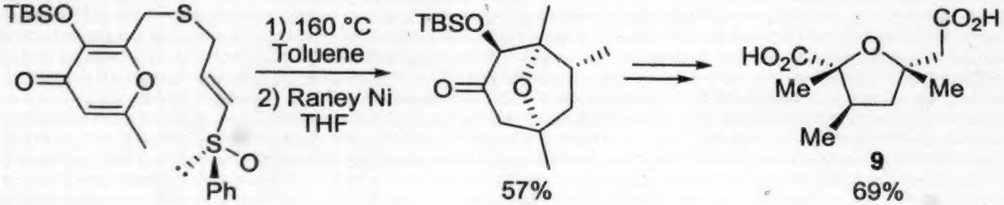
Mascarenas has reported a fascinating metal-free [5+2] cycloaddition[56-67] which couples a 5-carbon 3-oxidopyrylium fragment with a tethered olefin in a diastereoselective manner (Scheme **1.4**). The oxidopyrylium is generated *in situ*, either from base-treatment of a 6-acetoxy-3-pyranone, or by thermolysis of a 3-tributylsiloxy-4-pyrone. In the majority of examples, the olefin is tethered, at least temporarily, to the oxidopyrilium, although in a recent intermolecular example,[64] a cyclopropene acetal has been used.

Scheme 1.4



Tethers incorporating chiral functionalities such as sulfoxides and sulfoximes have been employed in an effort to probe the potential enantioselectivity of this process, and this work has culminated in the recent synthesis of enantiopure (+)-nemorensic acid **9**, Scheme **1.5**.[66] Ironically, it is the five-membered ring that is the ultimate target of this natural product synthesis; the seven-membered ring is cleaved in two steps subsequent to the [5+2] reaction.

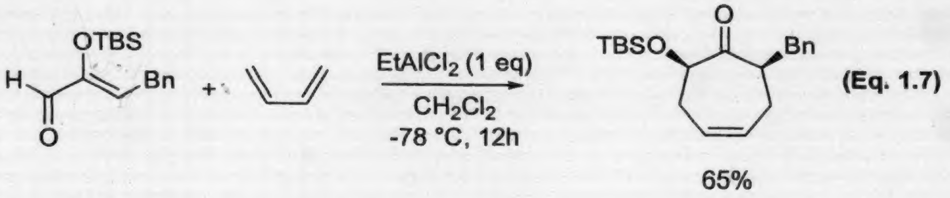
Scheme 1.5



Part D: Recent Developments in [4+3] Cycloaddition Methodology

Perhaps the most familiar example of the [4+3] cycloaddition is the reaction between dienes and a 3-carbon oxyallyl dienophile to generate a cyclohept-4-en-1-one. Major variations of this protocol differ primarily in the manner in which the oxyallyl species is generated. This reaction has been reviewed extensively elsewhere,[68-71] and for the most part need not be further discussed here.

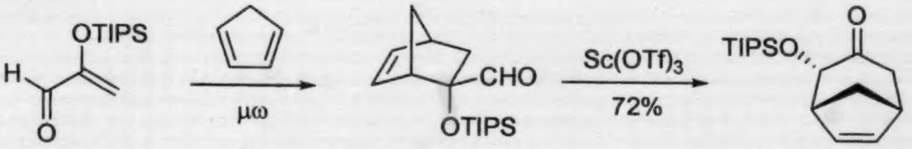
One variation of this reaction that has received considerable attention in the last few years, however, is the Lewis acid-catalyzed [4+3] cycloaddition of substituted acroleins and dienes. Although there were early reports of this reactivity more than 20 years ago,[72,73] there has been very little further development until recently because of the prevalence of a competing Lewis acid-promoted [4+2] Diels-Alder process. In 2000, however, Harmata[74] demonstrated the scandium triflate-catalyzed [4+3] cycloaddition of a siloxy-substituted acrolein with a range of dienes and furans. Funk[75] has more recently followed up with a report of similar reactivity in acroleins further substituted at the β-position; equation **1.7** presents a representative example of such a reaction. Apart from the parent butadiene, dienes successfully employed include 2-methylbutadiene,



pentadiene, cyclopentadiene, and furan. In the latter three cases, control of *endo*/*exo* selectivity remains an unresolved issue.

DFT analysis[76,77] of this reaction indicates that the annulation proceeds in a stepwise fashion. The calculations also indicate that the competing [4+2] reaction is reversible under the reaction conditions employed, and that the seven-membered ring [4+3] product is thermodynamically preferred. Davies[78] has reported experimental evidence for this, by inducing the [4+2] reaction by microwave irradiation, and then demonstrating that the [4+2] cycloadduct **10** converts to the [4+3] product **11** under Lewis-acidic conditions (Scheme **1.6**). Davies has also realized the successful incorporation of simple alkyl substituted acroleins, without siloxy substituents.

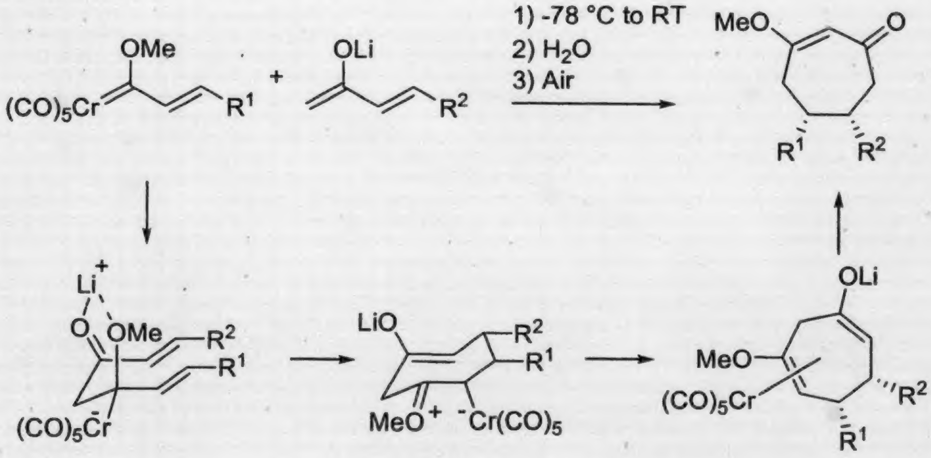
Scheme 1.6



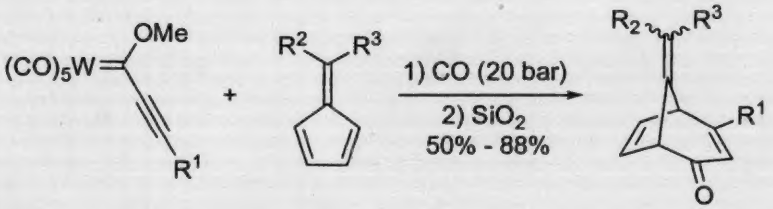
10 **11**

An interesting [4+3] cycloaddition of Fischer carbenes with methylvinyl ketone enolates has been reported by Barluenga.[79] The reaction furnishes cycloheptenones in modest (43% to 52%) yields in a process stoichiometric in chromium. A mechanism involving a 1,2 metal migration has been proposed (Scheme **1.7**), similar to his [5+2] reaction.[53]

Scheme 1.7

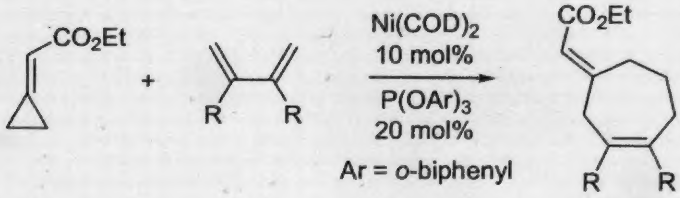


Additionally, Barluenga has reported a related [4+3] cycloaddition process incorporating various fulvenes as the 4-carbon component. The reaction must be carried out under a CO atmosphere in order to retard a competing cyclopropanation reaction, and yields range from 50% to 88% (Equation **1.8**).



(Eq. 1.8)

One other [4+3] cycloaddition to emerge very recently featured a Ni(0) catalyst.[80] Saito prepared seven-membered ring dienes bearing an exocyclic double bond via the cycloaddition of ethyl cyclopropylideneacetate **12** to a host of conjugated dienes (Equation **1.9**). Depending on the nature of the diene, yields range from 30% to 70% with respect to **12**; the diene is normally employed in severalfold excess. Although the yields are moderate at best, the method is catalytic with respect to nickel.



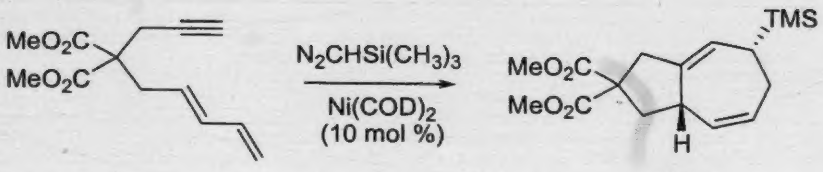
12

38-70%

(Eq. 1.9)

Part E: Recent Developments in Higher-Order Cycloaddition Methodology

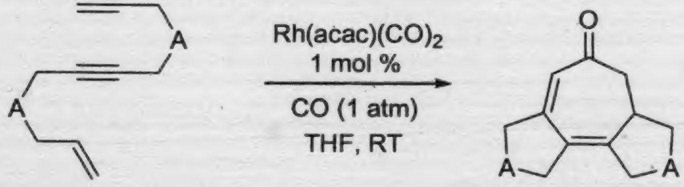
Montgomery has reported a three-component [4+2+1] pathway to seven-membered carbocycles via a nickel-catalyzed process.[81,82] The 1-carbon fragment is derived from trimethylsilyldiazomethane, and the 4-carbon and 3-carbon units arise, respectively, from diene and alkyne functionalities. In the examples reported, yields range from 45% to 78% (Equation **1.10**, for example). In all cases, the diene and alkyne moieties are tethered by a three-atom chain; bicyclic products such as **13** are thus obtained.



(Eq. 1.10)

13
76%, dr = 13:1

An interesting [2+2+2+1] process has been disclosed by Ojima,[83] which incorporates a carbonyl fragment into a seven-membered ring along with two alkyne fragments and an olefin (Equation **1.11**). Although the cycloadduct yields often range above 80% in this process, the methodology is so far limited to systems in which the alkyne and alkene moieties are tethered so that only polycyclic products are attainable. Nonetheless, the methodology is tolerant of heteroatoms in the tether, as well as several other carbon fragments.

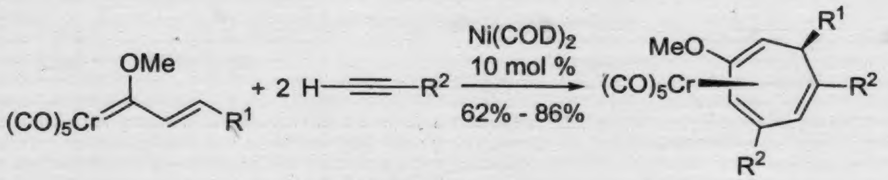


(Eq. 1.11)

A = O, NTs, N-*t*-boc, CR_2

50%-91%

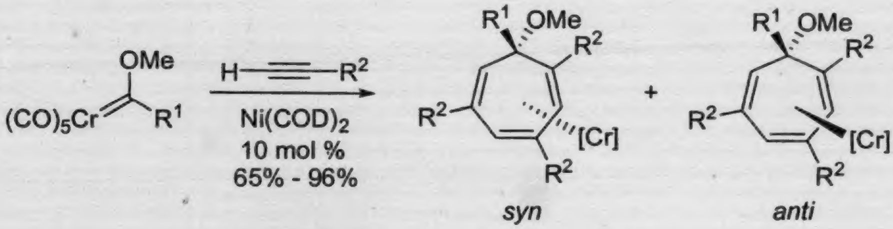
Barluenga has reported several carbene-based higher-order cycloaddition reactions in recent years. In 2003,[84] he described a Ni(0)-mediated [3+2+2] cycloaddition process incorporating Fischer vinylcarbenes and alkynes into seven-membered rings via a double insertion process (Equation **1.12**). Yields for this process are typically good, ranging from 62% to 86%. It is noteworthy that a β-substituted carbene (such as **14**) leads exclusively to the *endo* isomer **15** of the product, regardless of the stereochemistry about the olefinic double bond in **14**.


OMe
(CO)5Cr
R1
+ 2 H—≡—R2
Ni(COD)2
10 mol %
62% - 86%
MeO
(CO)5Cr
R1
R2
R2

(Eq. 1.12)

14 R^1 = Ph, 2-furyl, *n*-Pr, ferrocenyl
R^2 = alkyl or TMS **15**

A related [2+2+2+1] reaction was also reported at the same time by Barluenga,[84] generating a cycloheptatriene from three alkyne fragments and a Fischer carbene (**16**), also under Ni(0) mediation (Equation **1.13**). Yields range from 65% to 96%, and in the majority of cases, the *syn* isomer **17** comprises better than 90% of the whole.


OMe
(CO)5Cr
R1
H—≡—R2
Ni(COD)2
10 mol %
65% - 96%
R1
OMe
R2
R2
[Cr]
R2
syn
+
R1
OMe
R2
R2
[Cr]
R2
anti

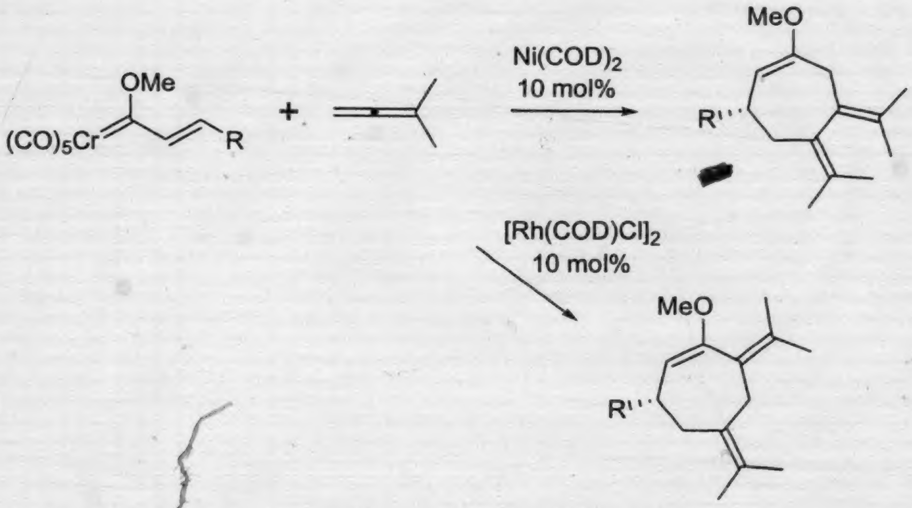
(Eq 1.13)

16 [Cr] = Cr(CO)$_5$
R^1 = alkyl or aryl
R^2 = alkyl or TMS **17** **18**

The [3+2+2] cycloaddition was also shown to be amenable to allene incorporation,[85] generating cycloheptenones bearing two exocyclic alkene functionalities.

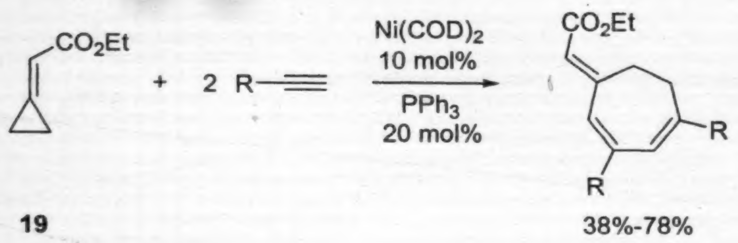
Interestingly, the relative positions of the two exocyclic double bonds were dependent on the nature of the catalyst employed (Scheme **1.8**). When catalyzed by Ni(COD)$_2$, the reaction produced 1,2-dialkylidene derivatives whereas 1,3-dialkylidene products were obtained from the otherwise identical reaction catalyzed by [Rh(COD)Cl]$_2$. Yields in either case were moderate, varying from 40% to 71%.

Scheme 1.8



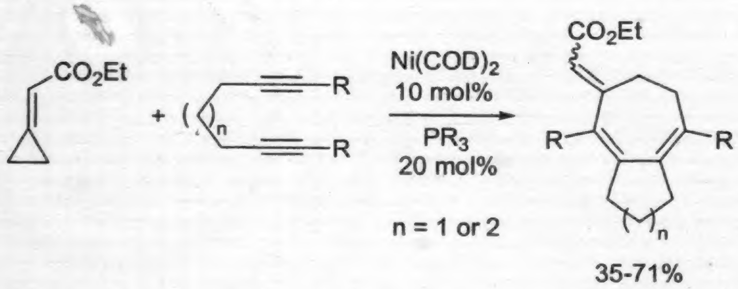
Another [3+2+2] cycloaddition has been developed by Saito[86] (Equation **1.14**) which renders cycloheptadiene products in moderate yields (30%-78%) from ethyl cyclopropylideneacetate **19** and alkynes in the presence of a catalytic amount of Ni(0); the conditions closely parallel those of Saito's [4+3] cycloaddition[80] (*vide supra*).

Saito has used the same methodology to prepare 7,6- and 7,5-fused bicyclic targets from tethered alkynes[87] (Equation **1.15**). Whereas the cycloaddition of non-tethered alkynes affords seven-membered rings with a single configuration about the


CO2Et
+ 2 R
Ni(COD)2
10 mol%
PPh3
20 mol%
CO2Et
R
R
19
38%-78%

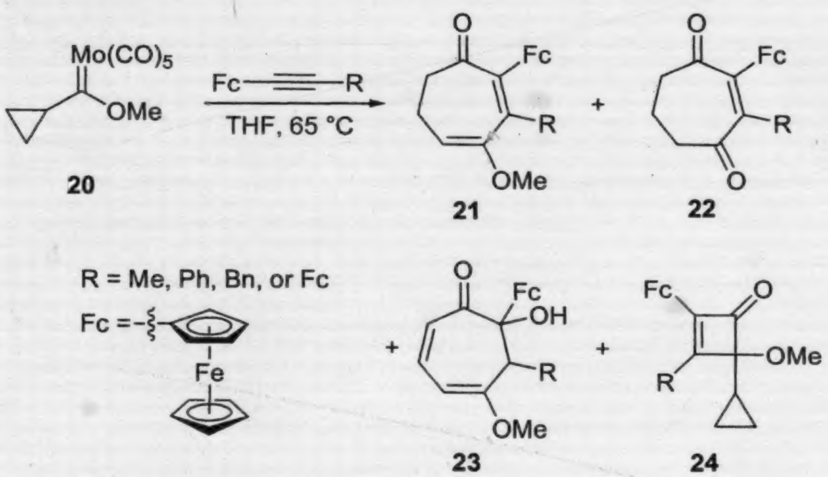
(Eq. 1.14)

exocyclic double bond (Equation **1.14**), the cycloadducts isolated from tethered alkynes were plagued with small amounts (10%-15% of the whole product) of the minor *Z* isomer.


CO2Et
+
n
R
R
Ni(COD)2
10 mol%
PR3
20 mol%
n = 1 or 2
CO2Et
R
R
n
35-71%

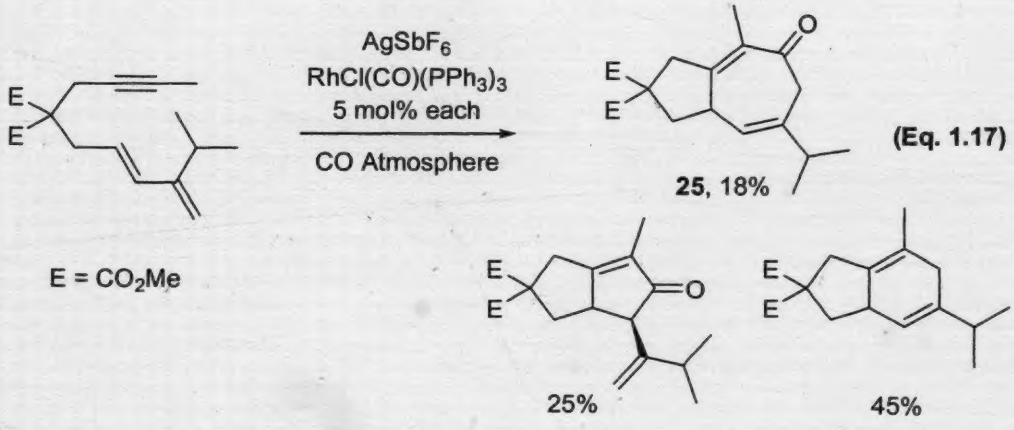
(Eq. 1.15)

One other [3+2+2] process has been described in 2007 by Zora,[88] in which interesting ferrocenyl alkynes are incorporated into seven membered rings (Equation **1.16**). At present, only a small number of alkynes have been incorporated and, in each case, a mixture of products has been recovered. Nonetheless, seven-membered ring formation appears to be efficient (combined yields of **21-24** exceed 70%) when only one terminus of the alkyne bears the ferrocenyl fragment.


Mo(CO)$_5$
OMe
20
Fc——R
THF, 65 °C
O
Fc
R
OMe
21
+
O
Fc
R
O
22
R = Me, Ph, Bn, or Fc
Fc =
Fe
+
O
Fc
OH
R
OMe
23
+
Fc
O
OMe
R
24

(Eq. 1.16)

Wender has disclosed a formal [4+2+1] process[89] that occurs as a side reaction during some attempted dienyl Pauson-Khand reactions (Equation **1.17**). To date, the [4+2+1] adduct **25** has appeared only as a minor product (less than 20%), although Wender has indicated that further studies are underway to better understand and facilitate this process.

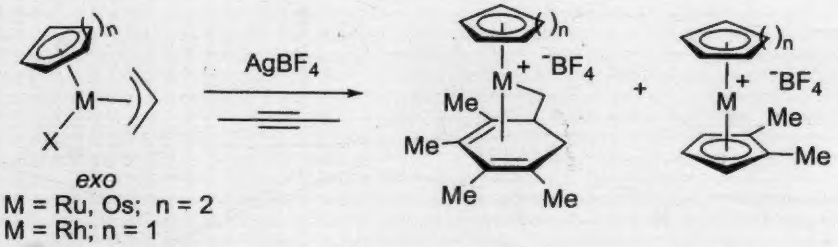

E
E
E = CO$_2$Me
AgSbF$_6$
RhCl(CO)(PPh$_3$)$_3$
5 mol% each
CO Atmosphere
E
E
O
25, 18%
(Eq. 1.17)
E
E
O
25%
E
E
45%

Chapter 2 – Bicyclic Organic Molecules From a Cobalt-Mediated [3+2+2] Cycloaddition

Section 1: Introduction

Part A: Cobalt-Mediated [3+2+2] Allyl/Alkyne Cycloadditions

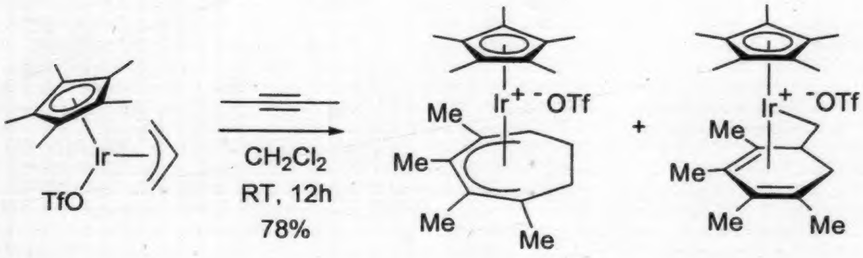
The first [3+2+2] double alkyne insertions were reported by Rubezhov[90,91] in 1988. In each case, the double insertion process furnished a six-membered ring organometallic fragment, along with a small amount of single insertion product (Equation **2.1**). Several metal templates (**26** - **28**) were employed; in each case a modest yield (32-49%) was obtained, and the scope of the reactivity was limited to 2-butyne. In no case was a seven-membered ring cycloadduct obtained.



26-28 **29** **30**

(Eq. 2.1)

In an effort to realize seven-membered ring formation, Schweibert and Stryker[92,93] employed a more sterically hindered and electronically enriched Cp*Ir(III) template **31** and, in doing so, prepared the cycloheptadienyl complex **32** as the major product upon addition of 2-butyne (Equation **2.2**). In this system, the six-membered ring cycloadduct **33** (analogous to Rubezhov's product **29**) was obtained as a minor product. A mechanistic proposal for the formation of products **32** and **33** will be presented later in this chapter.



31 **32** **33**

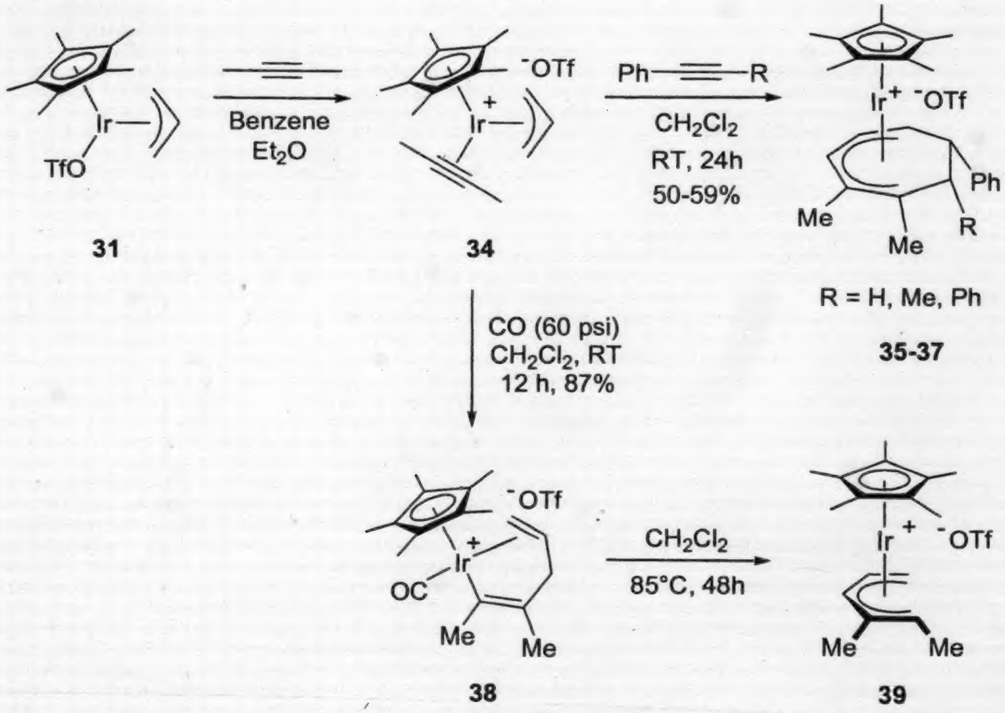
5 : 1

(Eq. 2.2)

Schweibert was also successful in the isolation of the presumed intermediate cationic allyl alkyne complex **34** by precipitation from a mixture of diethyl ether and benzene (Scheme **2.1**). The competency of this intermediate in the [3+2+2] cycloaddition was also demonstrated by subsequent conversion of **34** into several cycloheptadienyl products **35-37** in moderate yield upon treatment with alkyne.

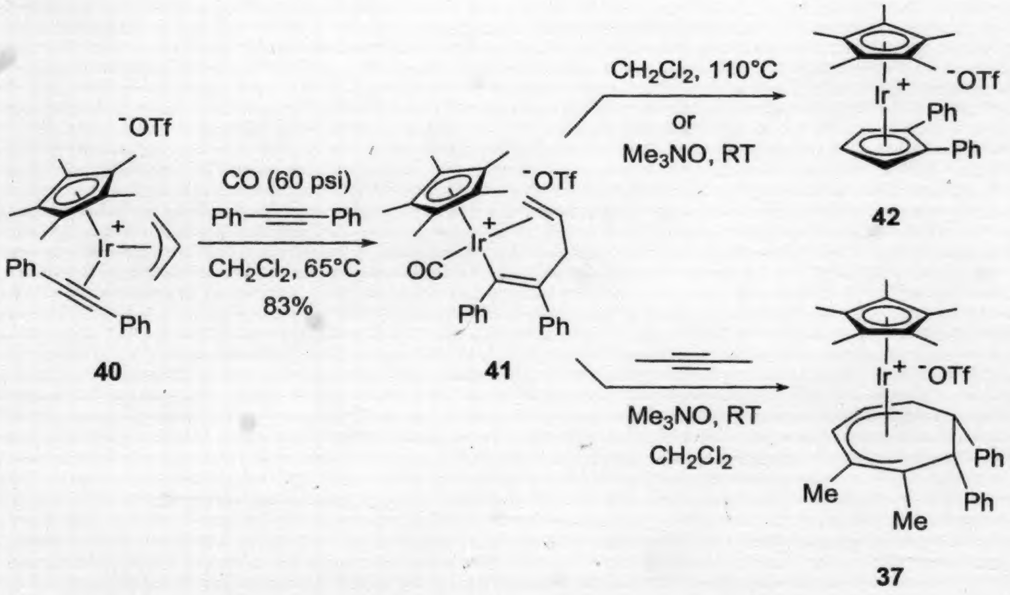
Further mechanistic insight was gained by Schweibert upon the trapping of vinyl olefin complex **38** as a carbonyl adduct, implicating a related *non-carbonylated* analogue of **38** as a potential intermediate on the pathway to cycloheptadienyl products. In the absence of a second equivalent of alkyne, the thermolysis of vinyl olefin **38** afforded the

Scheme 2.1

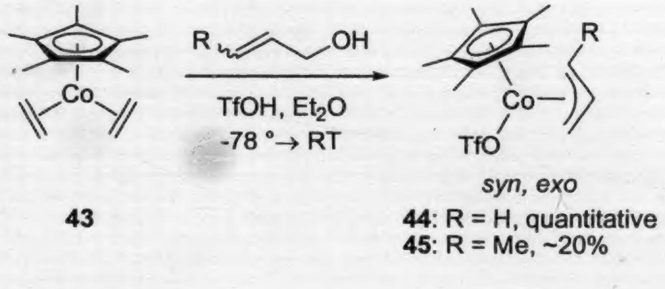

31
TfO
Ir
Benzene
Et₂O
34
-OTf
Ir
+
Ph—≡—R
CH₂Cl₂
RT, 24h
50-59%
Ir+ -OTf
Ph
R
Me
Me
R = H, Me, Ph
35-37
CO (60 psi)
CH₂Cl₂, RT
12 h, 87%
38
-OTf
OC
Ir
+
Me
Me
CH₂Cl₂
85°C, 48h
Ir + -OTf
Me
Me
39

open pentadienyl complex **39**. By contrast, thermolytic decarbonylation of the diphenyl species **41** (Scheme **2.2**) furnished the closed mixed iridacenium complex **42**; the same species was also isolated when the decarbonylation was promoted by trimethylamine *N*-oxide in the absence of additional alkyne. On the other hand, *N*-oxide-promoted decarbonylation of **41** furnished **37** when performed in the presence of additional 2-butyne, providing additional evidence for the intermediacy of the 16-electron non-carbonylated vinyl-olefin analogue of **38**.

Scheme 2.2


-OTf
+
Ir
Ph
Ph
40
CO (60 psi)
Ph—≡—Ph
CH2Cl2, 65°C
83%
-OTf
+
Ir
OC
Ph
Ph
41
CH2Cl2, 110°C
or
Me3NO, RT
Ir +
-OTf
Ph
-Ph
42
Me3NO, RT
CH2Cl2
Ir+ -OTf
Ph
Ph
Me
Me
37

Owing to the considerable expense associated with stoichiometic iridium chemistry, the focus of the investigation was shifted by Etkin[94,95] to encompass the related cobalt-centered templates. The requisite Cp*Co(III) allyl starting materials were prepared in several ways. The parent allyl complex **44** was recovered quantitatively upon reaction of bis(ethylene) complex **43** with allyl alcohol under protolytic conditions (Equation **2.3**).

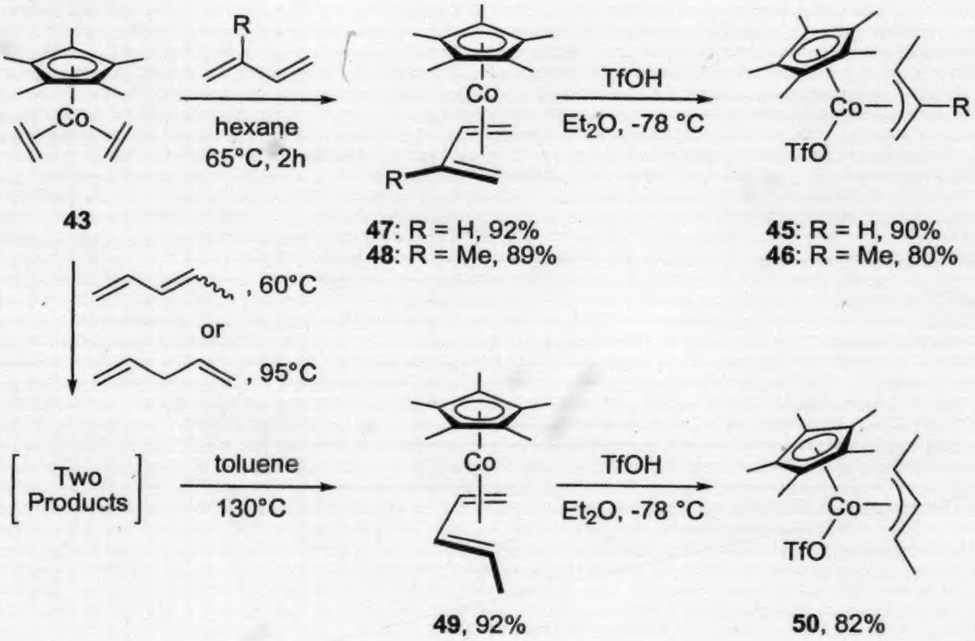

Co
R
OH
TfOH, Et2O
-78 °→ RT
Co
TfO
R
syn, exo
43
44: R = H, quantitative
45: R = Me, ~20%

(Eq. 2.3)

Krivykh[96,97] had previously prepared the CpCo(III) analogue in this manner. Although substituted allyl complexes were successfully prepared in related manganese systems,[96-100] efforts to generate substituted Cp*Co(III) allyl complexes such as **45** proved fruitless.

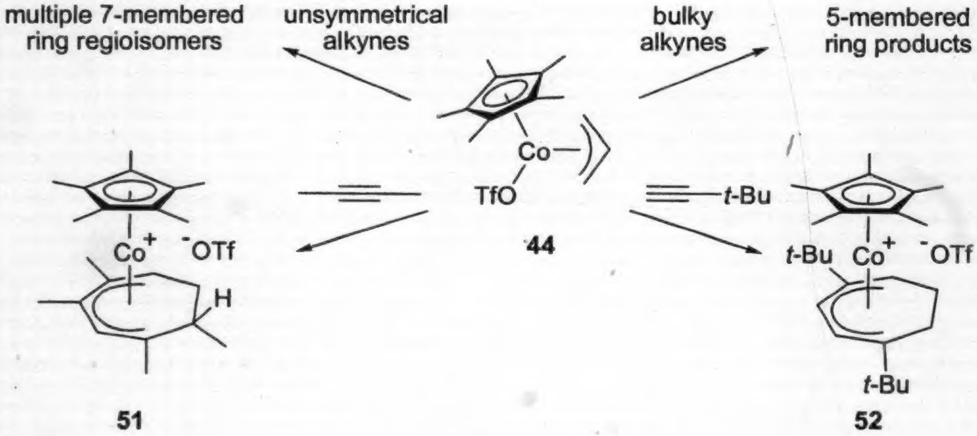
As substituted allyl substrates were not accessible via this direct protonolysis pathway, such complexes were instead furnished from **43** in two steps, via isolable Cp*Co(I) diene complexes (Scheme **2.3**).

Scheme 2.3

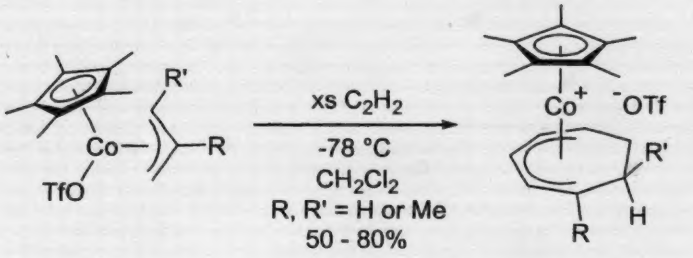

R
hexane
65°C, 2h
Co
R
TfOH
Et2O, -78 °C
Co
R
TfO
43
47: R = H, 92%
48: R = Me, 89%
45: R = H, 90%
46: R = Me, 80%
, 60°C
or
, 95°C
Two Products
toluene
130°C
Co
TfOH
Et2O, -78 °C
Co
TfO
49, 92%
50, 82%

The reactivity of these Cp*Co(III) allyl complexes with mono- and disubstituted alkynes was investigated by Etkin (Scheme **2.4**). Whereas only products containing undesired five-membered rings were isolated as primary products from reactions of parent allyl complex **44** with bulky alkynes (4,4-dimethyl-2-pentyne, diphenylacetylene, or trimethylsilylacetylene), the more desirable Cp*Co(III) cycloheptadienyl complexes were formed upon treatment of **44** with 2-butyne or 3,3-dimethyl-1-butyne. The structure of the 2-butyne adduct **51** was surprising; the position of the unsubstituted carbons in the seven-membered ring could only arise as a result of some previously unknown carbon-carbon bond activation,[101-103] which was further investigated by Dzwiniel and will be described in greater detail in chapter 4 of this thesis. In contrast to the partial success of **44** in [3+2+2] chemistry, crotyl complex **45** yielded only 5-membered ring products upon cycloaddition with substituted alkyne in excess.

Scheme 2.4


multiple 7-membered ring regioisomers
unsymmetrical alkynes
bulky alkynes
5-membered ring products
Co
TfO
44
t-Bu
Co+
-OTf
H
51
t-Bu
Co+
-OTf
t-Bu
52

The allyl complexes **44**, **45**, and **46** each furnished seven-membered ring cycloadducts upon treatment with acetylene (Equation **2.4**); this reactivity is in stark contrast with the failure of the analogous iridium complexes to yield the corresponding cycloheptadienyl targets. Although the Cp*Co(III) cycloheptadienyl products were only partially characterized by Etkin, preliminary NMR investigation was strongly suggestive of the product structures **53-55**, indicating that the Cp*Co(III) motif was indeed a promising template for preparative [3+2+2] cycloadditions.



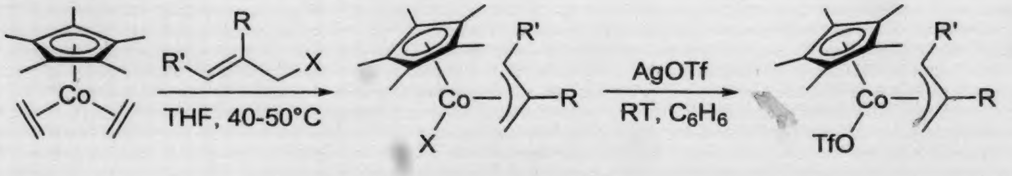
44 - 46

53 - 55

(Eq. 2.4)

The cycloheptadienyl complexes **53-55** were ultimately characterized by Dzwiniel, who greatly extended the scope and understanding of this [3+2+2] cycloaddition over the course of his Ph.D. research.[17,95,101-103] A number of elaborated Co(III) allyl complexes were accessed oxidatively by Dzwiniel from the ubiquitous Cp*Co(I) bis-ethylene complex **43** (Scheme **2.5**). Although several Cp*Co(III) allyl complexes were isolated as triflates following a silver ion metathesis, the majority of the allyl complexes prepared oxidatively by Dzwiniel were characterized and stored as the halides owing to the relative thermal instability of the corresponding triflates. Silver ion was normally employed *in situ* for the requisite halide ion abstraction in subsequent [3+2+2] cycloadditions; silver triflate and silver tetrafluoroborate were both proficient in the *in situ* counterion metathesis.

Scheme 2.5


Co
R
R'
X
THF, 40-50°C
R'
Co
R
X
AgOTf
RT, C_6H_6
R'
Co
R
TfO

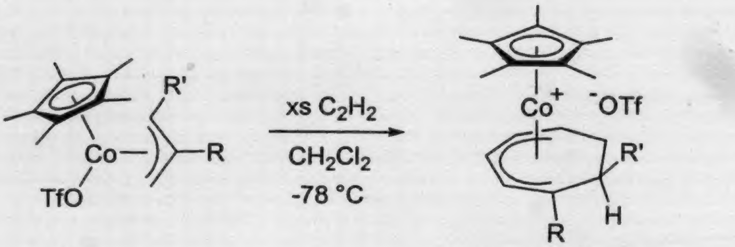
43

56: R,R' = Me,H, X = Cl, 71%
57: R,R' = H,Ph, X = Cl, 70%
58: R,R' = H,CO_2Me, X = Br, 82%

45: R,R' = Me,H, 89%
59: R,R' = H,Ph, 76%

In a few cases, Dzwiniel demonstrated the use of the Co(III) allyl halides directly as [3+2+2] substrates by using 2,2,2-trifluoroethanol as solvent; the strongly ionizing nature of this solvent circumvented the requirement of a weakly coordinating counter-ion such as triflate.

Whereas Cp*Ir(III) allyl complexes failed to furnish isolable [3+2+2] cycloadducts upon treatment with terminal alkynes or acetylene, the corresponding Cp*Co(III) allyl analogues were amenable to [3+2+2] cycloadditions with these alkynes (Equation **2.5**). Dzwiniel isolated several Cp*Co(III) cycloheptadienyl complexes upon


R'
Co
R
TfO
xs C_2H_2
CH_2Cl_2
-78 °C
Co^+
^-OTf
R'
H
R

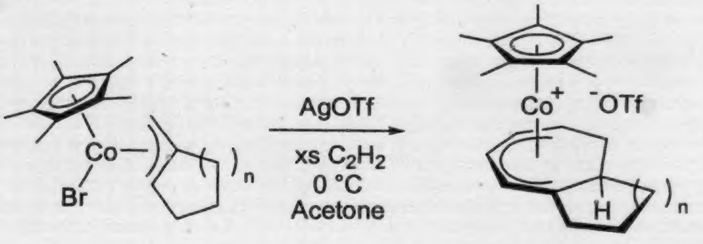
(Eq. 2.5)

44 - 46

53: R = R' = H, 52%
54: R = H, R' = Me, 79%
55: R = R' = Me, 67%

dissolution of the allyl precursor in a saturated dichloromethane solution of acetylene. These same products had been prepared previously by Etkin, but had not been fully characterized.

The interesting bicyclic products **60** and **61** were also prepared by an *in situ* halide abstraction (Equation **2.6**). Complex **60** is notable in that it was the first Co(III) cycloheptadienyl species for which X-ray crystallographic analysis was successful.



60: n = 1, 52%
61: n = 2, 79%

(Eq. 2.6)

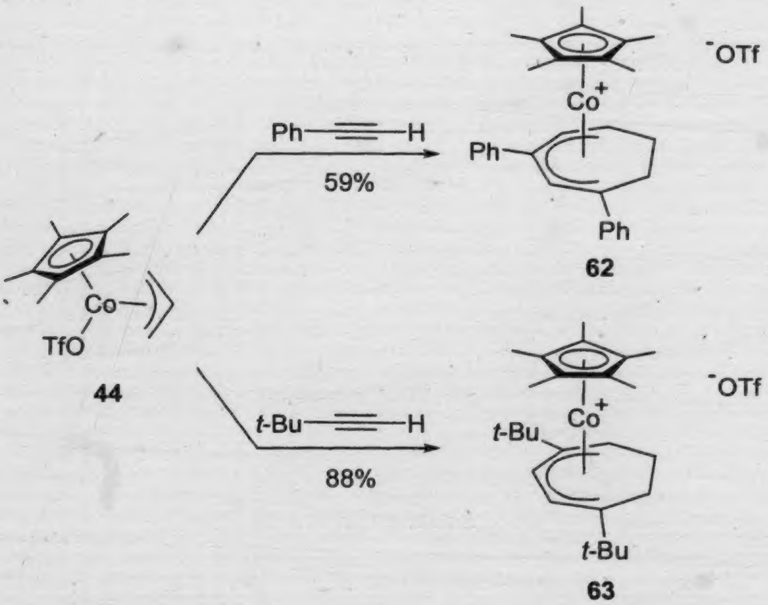
In many cases, Dzwiniel was able to obtain analytically pure products by careful (and sometimes repeated) silica gel chromatography employing dichloromethane as solvent with a small amount (typically 2% - 5% by volume) of methanol present as co-solvent. Under these chromatographic conditions, any undesired [3+2] cycloadduct byproducts had no appreciable mobility and thus remained at the top of the column. As a consequence of this purification, many of Dzwiniel's cycloadducts are fully characterized; a very thorough account of the NMR spectroscopy of Co(III) cycloheptadienyl complexes appears in Dzwiniel's Ph. D. dissertation.

In particular, Dzwiniel was able to unambiguously establish the regiochemistry of the reaction with respect to the fate of allyl substituents. In a "normal" [3+2+2] cycloaddition, a substituent at the terminus of the allyl fragment (i.e. R′ in Equation **2.5**) was placed on a saturated carbon in the resultant cycloheptadienyl product. Likewise, a substituent at the central position of the allyl fragment (i.e. R in Equation **2.5**) selectively traced to the unsaturated pentadienyl terminus of the resultant cycloheptadienyl ligand. The only exceptions to this pattern were exhibited in the so-called "anomalous" [3+2+2] cycloadditions of the type first observed by Etkin, in which a novel carbon-carbon bond activation mechanism fragments the allyl moiety during the cycloaddition process.

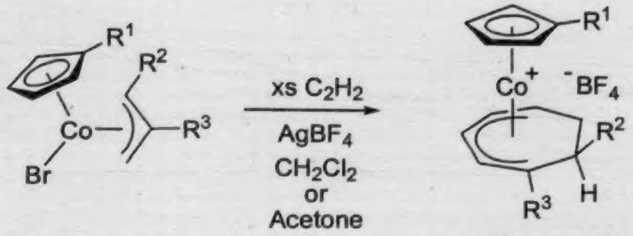
In those cases in which the allyl fragment was terminally substituted, Dzwiniel established the stereochemistry of the saturated product carbon which bore this substituent by careful NOE experiments, as well as X-ray crystallography of complex **60**. In all known cases, the substituent (ie R′ in Equation **2.5**) is installed on the cycloheptadienyl fragment in an *endo* configuration, on the face of the ring proximal to the metal. Still further evidence for the *endo* stereochemistry of this substituent was provided by comparison of [3+2+2] cycloadduct **54** with its corresponding *exo* diastereomer, which was obtained by independent synthesis.

Cycloadditions with substituted alkynes were also evaluated by Dzwiniel. Interestingly, unsymmetrically substituted alkynes proceeded to single cycloadducts with high regioselectivity, although the actual substitution pattern obtained varies depending on the substituent; this effect is exemplified by comparing the products obtained from the cycloadditions of *t*-butylacetylene and phenylacetylene (Scheme **2.6**). Although Dzwiniel invokes steric and electronic arguments to explain this discrepancy, the precise reason for the disparate regioselectivities has not been clearly established.

Scheme 2.6



Dzwiniel also extended the scope of the [3+2+2] reaction to include Co(III) templates with ancillary ligands other than Cp* in an effort to identify the ideal balance of steric and electronic templating factors. Owing in part to its low cost and high availability, the parent unsubstituted cyclopentadienyl ligand was of particular interest; the simple methylcyclopentadienyl ligand was likewise investigated by Dzwiniel. A series of these Co(III) allyl substrates were productive in [3+2+2] cycloaddition chemistry although, for the most part, Dzwiniel limited his investigation of these templates to reactivity with acetylene (Equation **2.7**).



(Eq. 2.7)

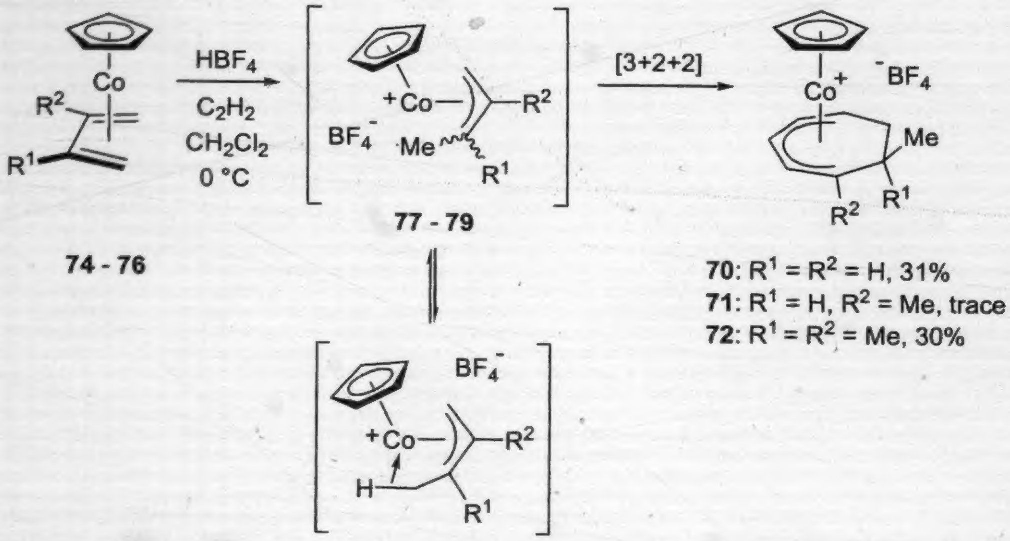
64 - 68

69: $R^1 = R^2 = R^3 = H$, 47%
70: $R^1 = R^3 = H$, $R^2 = Me$, 69%
71: $R^1 = H$, $R^2 = R^3 = Me$, 58%
72: $R^1 = Me$, $R^2 = R^3 = H$, 73%
73: $R^1 = R^2 = Me$, $R^3 = H$, 33%

The 1,1,2-trimethylallyl complex **79**, which may in fact be best described as an agostic allyl complex, was formed *in situ* upon protonation of **76** ($R^1 = R^2 = Me$) and led to the first example of successful [3+2+2] cycloaddition using a complex doubly substituted at one terminus (Scheme **2.7**). This result is significant in that the cycloaddition must have involved carbon-carbon bond formation at a sterically encumbered fully-substituted site to furnish a quaternary center.

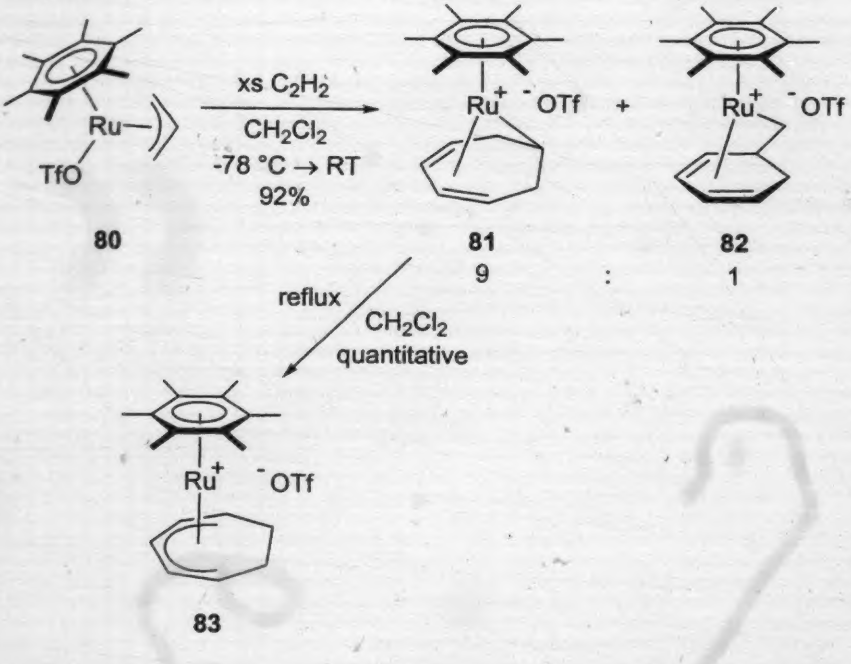
Concomitant with Dzwiniel's investigation of Co(III) substrates for [3+2+2] cycloaddition, Older[104] demonstrated analogous reactivity on a related ruthenium template (Scheme **2.8**). Although the majority of alkynes afforded only 5-membered ring products upon reaction with arene Ru(II) allyl triflate **80**, several alkynes did proceed in a [3+2+2] manner to give seven-membered rings. Notably, two equivalents of acetylene were incorporated into allyl complex **80**, resulting in a mixture of cyclic double insertion products **81** and **82**. The fluxional σ-diene complex **81** further proceeded to η^5-cycloheptadienyl complex **83** slowly upon standing at room temperature or more rapidly when heated to 60 °C.

Scheme 2.7


Co
HBF$_4$
C$_2$H$_2$
CH$_2$Cl$_2$
0 °C
R^2
R^1
74 - 76
+Co
BF$_4^-$
Me
R^2
R^1
77 - 79
[3+2+2]
Co$^+$
$^-$BF$_4$
Me
R^1
R^2
BF$_4^-$
+Co
H
R^2
R^1

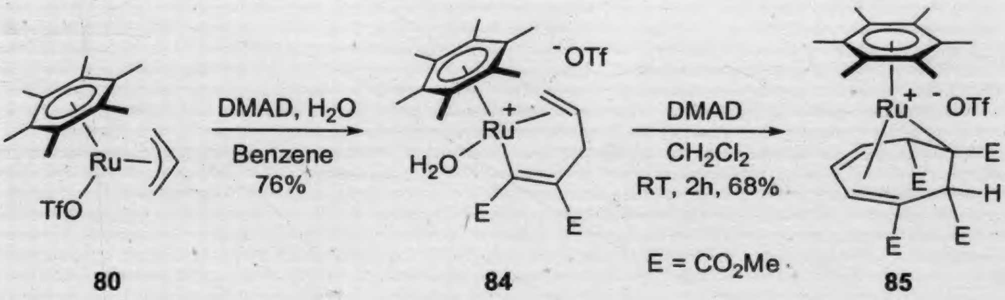
70: $R^1 = R^2 = H$, 31%
71: $R^1 = H$, $R^2 = Me$, trace
72: $R^1 = R^2 = Me$, 30%

Scheme 2.8


Ru
TfO
80
xs C$_2$H$_2$
CH$_2$Cl$_2$
-78 °C → RT
92%
Ru$^+$
$^-$OTf
+
Ru$^+$
$^-$OTf
81
9
:
82
1
reflux
CH$_2$Cl$_2$
quantitative
Ru$^+$
$^-$OTf
83

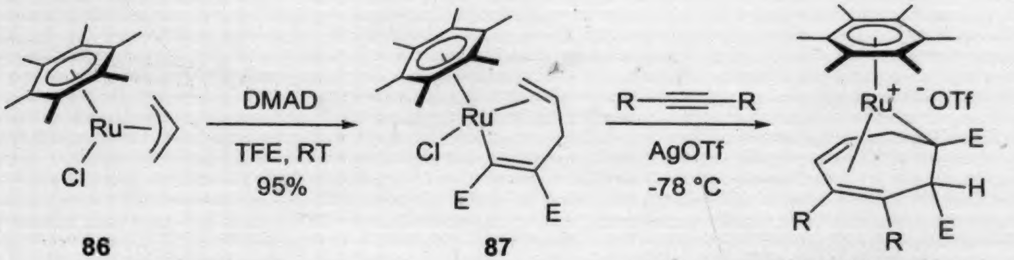
A very interesting result was observed by Older, using dimethyl acetylenedicarboxylate (DMAD) as the alkyne (Scheme **2.9**). Whereas this electron-deficient alkyne is unreactive in the related Co(III) and Ir(III) allyl systems, with ruthenium the reaction of one equivalent of DMAD proceeds cleanly to vinyl olefin complexes when added to a ruthenium template. Older explored two variations on this theme: in the first case, the cationic aquo complex **84** was isolated from the aryl Ru(III) allyl triflate precursor **84** (Scheme **2.9**).

Scheme 2.9



Alternatively, the neutral chloride complex **87** was isolated in high yield from addition of DMAD to aryl Ru(III) allyl chloride **86** (Scheme **2.10**). In either case, seven membered-ring products were accessible upon the introduction of additional alkyne; the fact that vinyl olefin complexes were competent intermediates in the [3+2+2] cycloaddition process echoed the earlier Ir(III) vinyl olefin chemistry reported by Schweibert (Schemes **2.1** and **2.2**).

Scheme 2.10



86 **87**

88: R = Me, ~81%
89: R = -$(CH_2)_6$-, 63%
90: R = H, 57%

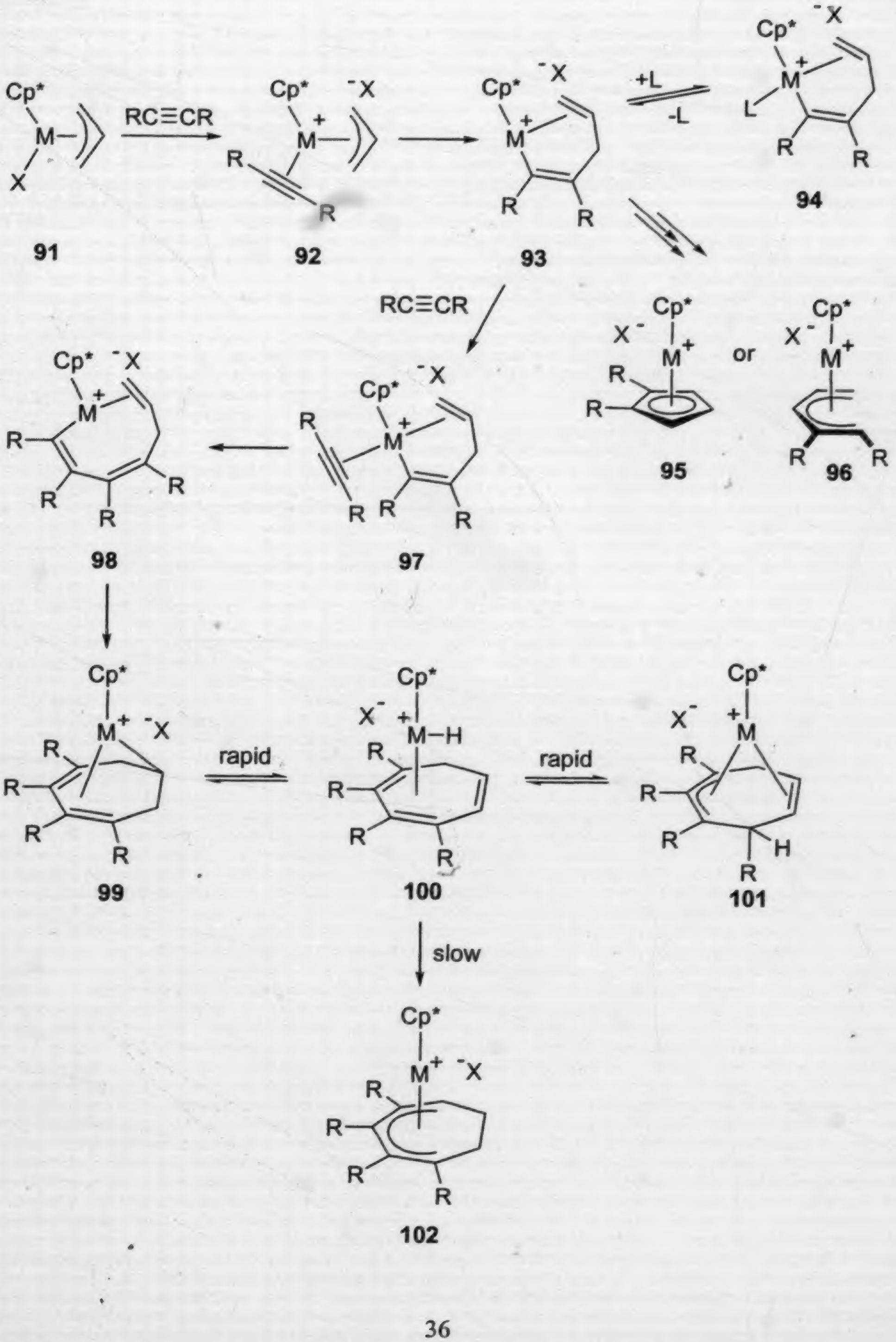
E = CO_2Me

Over time, a probable mechanistic pathway for the cobalt-mediated [3+2+2] cycloaddition has emerged based, in part, on intermediates and reactivities that have been established using Ir and Ru templates. A very thorough discussion of this pathway appears in Dzwiniel's dissertation[105] and is merely summarized here (Scheme **2.11**).

In the initial step, a coordination site is made available by dissociation of the weakly coordinating counterion. Upon subsequent coordination of an alkyne, the cationic allyl alkyne intermediate **92** is formed. Although no such cobalt complex has been isolated, the iridium and ruthenium anologues have been isolated and characterized by Schwiebert and Older respectively.

The 18-electron allyl alkyne intermediate species **92** proceeds to a 16-electron vinyl olefin intermediate **93** via migratory insertion of the alkyne fragment into the carbon-metal bond of **92** at one end of the allyl ligand. Evidence for the intermediacy of this complex is implied by the isolation of the carbonylated iridium analogues **38** and **41** by Schwiebert (*vide supra*); no such species has been directly observed in cobalt

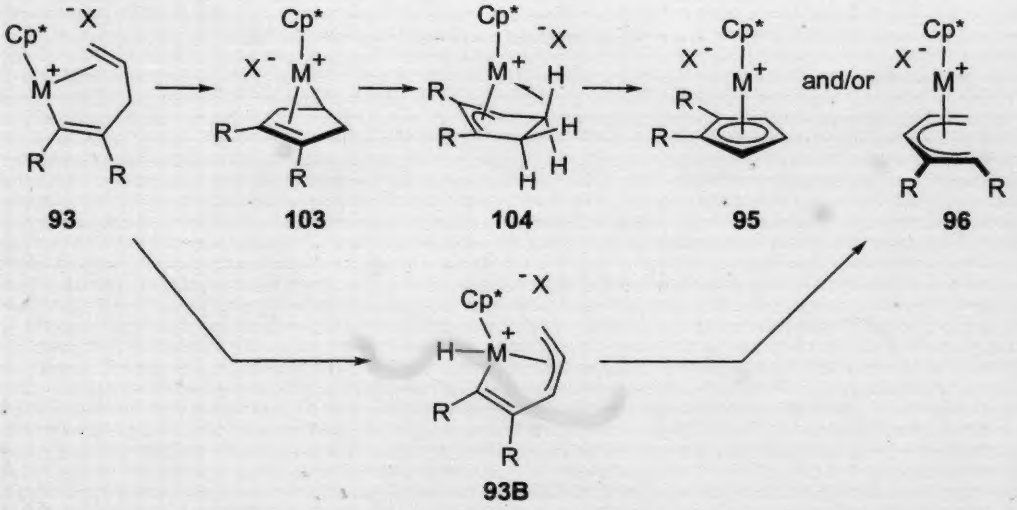
Scheme 2.11


Cp*
M
X
RC≡CR
-X
+
R
91
92
93
+L
-L
L
94
95
or
96
97
98
99
rapid
M–H
H
100
101
slow
102

chemistry as subsequent steps appear to be much faster than the formation of complex **93**. The intermediacy of analogues **84** and **87** in the parallel ruthenium chemistry provides further support for the transient formation of **93**.

Depending on the specific reaction conditions employed, the pathway could proceed from **93** either to product or to the two single insertion by-products **95** or **96** that are often competitively formed. If coordination of a second equivalent of alkyne is retarded as a result of steric constraints or low alkyne concentration, σ,π-cyclopentenyl complex **103** is formed and then proceeds via allyl agostic complex **104** either to open pentadienyl complex **95** or to cobaltacenium complex **96** (Scheme **2.12**); an allyl agostic complex similar to **104** has been isolated by Spencer, and its subsequent rearrangements have been well characterized in Spencer's chemistry, the relative amount of closed cyclopentadienyl product and open pentadienyl product is primarily influenced by the absence or presence of small amounts of adventitious water.

Scheme 2.12

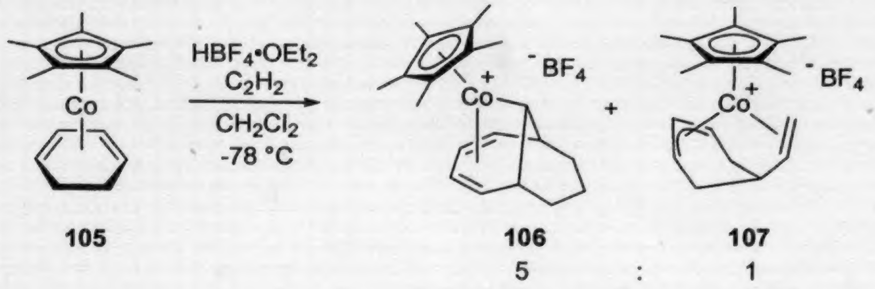


A perhaps more likely pathway for the formation of open pentadienyl by-product **96** (but not for **95**) proceeds via an allylic hydride activation in **93** to furnish allyl vinyl intermediate **93B**, which proceeds directly to **96** upon elimination.

On the other hand, if a second equivalent of alkyne is allowed to coordinate to vinyl olefin complex **93**, a second alkyne insertion may occur (Scheme **2.11**). Although the proposed vinyl bis-olefin intermediate **98** has never been directly isolated or observed, it is the intuitively obvious immediate precursor to σ-diene complexes such as **99**.

The regiochemistry of the migratory annulation of intermediate **98** is strongly influenced by the steric and electronic profile of the metal template. In most related systems, this insertion furnishes primarily six-membered rings, a reflection of the kinetic favorability of migration to the internal alkene carbon to make rings of this size. Even in those ruthenium systems that yield seven membered rings, small amounts of six-membered ring byproduct can be formed in significant amounts.

The first examples of seven-membered ring complexes exhibiting the σ-diene hapticity of complex **99** were reported by Older;[104] ruthenium complexes such as **81**, **85**, and **88-90** were isolated as double insertion products from Ru(III) allyl precursors. Chan[106] has since isolated and characterized a bridged bicyclic Co(III) σ-diene complex as an arrested intermediate along the [3+2+2] pathway (Equation **2.8**); the bridgehead hydrogen atoms in complex **106** are presumably unable to attain a conformation amenable to subsequent β-hydride elimination.



(Eq. 2.8)

The conversion of σ-diene intermediates into the observed conjugated η^5-cycloheptadienyl products **102** proceeds through a rapid sequence of hydrogen atom elimination-reinsertion steps which have been probed in great detail by Dzwiniel and Etkin via deuterium labeling studies. Upon activation of a β-hydrogen atom, the cationic triene hydride **100** is formed. From this intermediate, the hydride could, in principle, be placed at any of the six olefinic carbons, of which only four are likely to be coordinated to the metal at any one time. Deuterium labeling studies have shown that re-insertion to carbon two (or five) of the triene fragment occurs very rapidly from **100**, although none of the non-conjugated products from these insertions are ever isolated; hydrogen reactivation from any of these intermediates is also rapid and reversible. It is worth noting that reinsertion to carbon-2 regenerates intermediate **99**. Depending on the substitution pattern of **100**, competitive insertion at carbon-5 might generate a σ-diene complex substituted differently from **99** and thus open a pathway for the ultimate generation of multiple regioisomers of **102**.

It is also noteworthy that hydride insertion to carbon-3 or carbon-4 of **100** would produce an η^3-,η^2-cycloheptadienyl species akin to **101**. It is not clear whether such a species is formed reversibly during the ultimate formation of **102**, but recent work on a related [5+2] cycloaddition (Chapter 4 of this thesis) has revealed that cycloheptadienyl complexes exhibiting the "interrupted" η^3-,η^2- hapticity are often stable or semi-stable under [3+2+2] conditions. As no such η^3-,η^2-cycloheptadienyl complex **101** has ever been recovered from a [3+2+2] reaction, it is unlikely that **101** is formed from **100** under [3+2+2] conditions.

Ultimately, insertion from a triene hydride intermediate such as **100** places the hydride at a terminal olefin carbon; although this insertion occurs more slowly than insertion at an internal position, it occurs irreversibly. Co(III) η^5-cycloheptadienyl complexes **102** are completely resistant to thermal isomerization via β-hydride elimination.

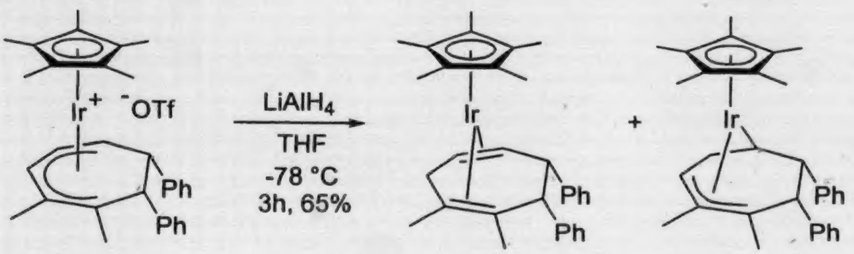
It is worth noting that the σ-diene complexes isolated by Older also ultimately proceed to conjugated products upon standing; at slightly elevated temperatures, the process is accelerated. The rapid interconversion between the σ-diene form (analogous to **99**), and the triene hydride form (analogous to **100**) was confirmed by Older by a series of spin saturation transfer experiments. All hydrogen atoms except for the two methylene hydrogens on the opposite face of the seven-membered ring from the metal were involved in the exchange process.

Part B: Nucleophilic Elaboration and Oxidative Decomplexation of Cycloheptadienyl Ligands

The electrophilicity of the cycloheptadienyl [3+2+2] cycloadduct has been probed by Dzwiniel, Etkin, and Schwiebert with an eye to further elaboration of the seven-membered ring.

The reaction chemistry in the cycloheptadienyl manifold has been most extensively studied on iron templates;[107-110] the same is true for the chemistry of the related open pentadienyl ligand. A number of factors influence the reactivity patterns of such complexes, including the formal charge and oxidation state of the metal, the strength and nature of the nucleophile, as well as the nature of any ancillary ligands on the metal center. In the case of iron η^5-pentadienyl complexes, softer nucleophiles selectively add to the terminus of the pentadienyl fragment whereas harder nucleophiles, such as alkyllithium reagents, typically select for reaction at the C-2 position to furnish a η^1-η^3 σ-allyl cycloheptendiyl. These reactivity patterns are in partial accordance with the selectivities predicted by the often incorrect DGM rules,[111] although these rules do not predict the formation of any C-2 adduct.

In the case of Cp*Ir(III) cycloheptadienyl complexes of the sort investigated by Schwiebert,[93] the DGM rules also appear to be only partially applicable. The addition of hydride furnishes a mixture of products (Equation **2.9**), of which the central carbon adduct **108** is the major constituent. Only a small amount of C-2 adduct **109** is detected and C-1 adduct is absent from the product matrix.

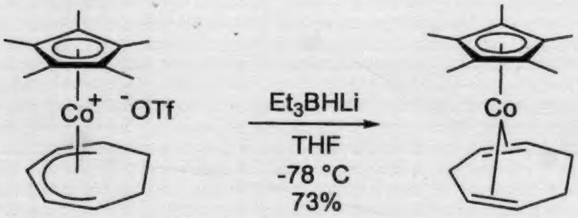


(Eq. 2.9)

37 **108** **109**

7 : 1

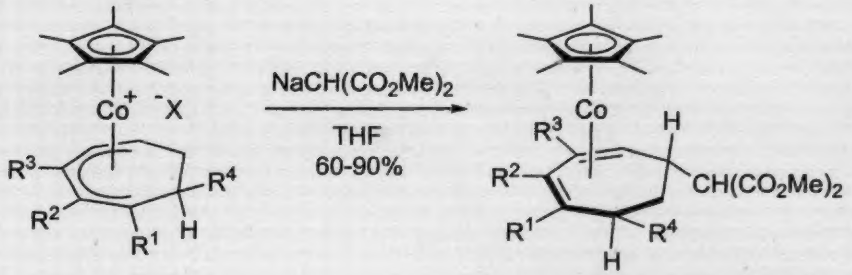
Prior to Dzwiniel's investigation, some reports of Cp*Co(III) cycloheptadienyl reactivity patterns were available. Weaker nucleophiles, such as stabilized carbanions or phosphines,[111-113] select for the terminus of the η^5-pentadienyl fragment. In contrast, harder nucleophiles such as hydride render central-carbon adducts (Equation **2.10**).[94,114,115] Etkin isolated the nonconjugated central carbon adduct **110** as the sole product from lithium triethylborohydride addition to the parent Cp*Co(III) cycloheptadienyl complex **53**.[94] Competitive single-electron reduction to furnish paramagnetic Co(II) products is often problematic when very basic carbon nucleophiles are employed.



(Eq. 2.10)

53 **110**

Dzwiniel successfully added malonate ion to several Co(III) cycloheptadienyl substrates (Equation **2.11**). In all cases in which an adduct was formed, addition occurred exclusively at the terminus of the conjugated system. Although a clear selectivity pattern was established, it was not determined whether or not this selectivity was as a result of a kinetic preference for the terminus or a thermodynamic preference for the conjugated Cp*Co(I) cycloheptadiene products **111-115**. The latter are expected to be more stable than less-conjugated alternatives owing to the greater backbonding capabilities of the conjugated π-system.



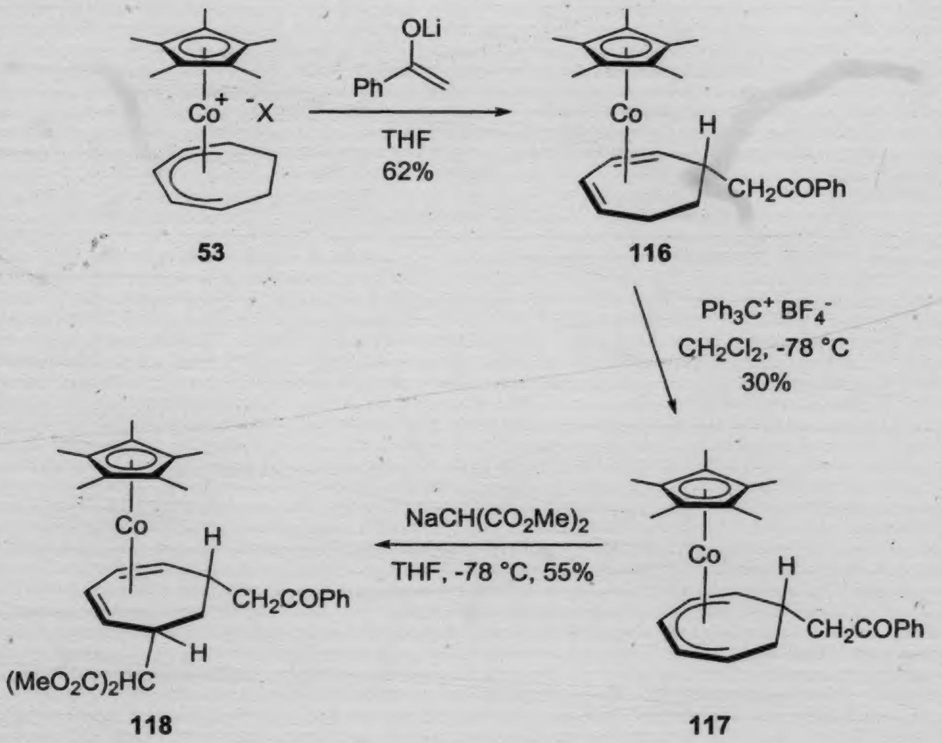
(Eq. 2.11)

111: $R^1 = R^2 = R^3 = R^4 = H$, $X = BF_4$
112: $R^1 = R^4 = H$, $R^2 = R^3 = Me$, $X = OTf$
113: $R^1 = R^2 = R^3 = H$, $R^4 = Me$, $X = OTf$
114: $R^1 = R^4 = Me$, $R^2 = R^3 = H$, $X = OTf$
115: $R^1 = R^3 = Ph$, $R^2 = R^4 = H$, $X = OTf$

Dzwiniel also demonstrated the feasibility of iterative addition of more than one nucleophile by employing trityl cation to abstract a hydride atom from initial adduct **116** (Scheme **2.13**). Abstraction of hydride by trityl cation were sometimes plagued by low yields as a result of a competing oxidative decomplexation process.

One advantage of nucleophilic elaboration of cycloheptadienyl ligands is that the resultant Co(I) products are more amenable to ligand decomplexation by oxidative methods. The [3+2+2] cycloaddition would be of little utility to organic chemists if the seven-membered ring product could not be removed from the metal template in good yield. In addition, recovery of the metal template in a reusable form would also be of great benefit as the cyclization process is not catalytic. It is difficult to envisage a direct method for decomplexation of the cycloheptadienyl ligand from a cationic Co(III) template.

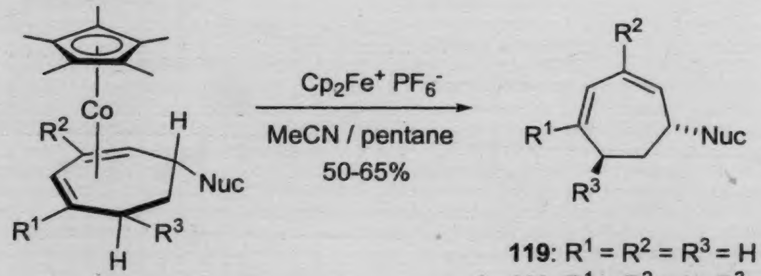
Scheme 2.13



Co
X
53
OLi
Ph
THF
62%
Co
H
CH₂COPh
116
Ph₃C⁺ BF₄⁻
CH₂Cl₂, -78 °C
30%
Co
H
CH₂COPh
117
NaCH(CO₂Me)₂
THF, -78 °C, 55%
Co
H
CH₂COPh
H
(MeO₂C)₂HC
118

Dzwiniel explored several methods for the removal of the organic cycloheptadienes from the Co(I) templates, including the use of the standard oxidants

$Ce(NH_4)_2(NO_3)_6$, $Pb(OAc)_4$, $FeCl_3$, and $CuCl_2$; unfortunately, none of these furnished decomplexed cycloheptadienes in greater than trace quantities. Eventually, Dzwiniel identified and developed a two-phase system that was productive in moderate yield, and the cobalt was recovered as $Cp^*Co(MeCN)_3^{2+}$ in yields greater than the recovery of the organic product (Equation **2.12**).

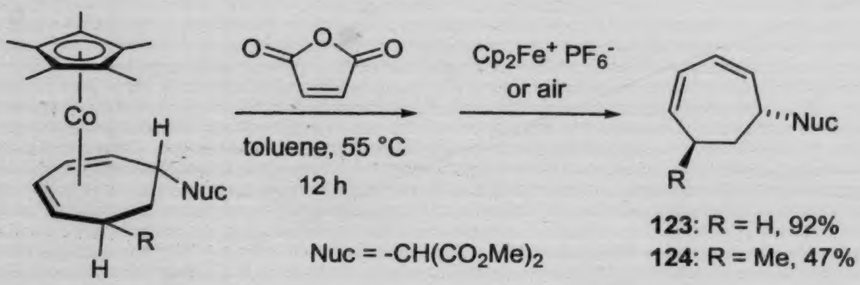

Co
R2
H
Nuc
R1
R3
H
Cp2Fe+ PF6-
MeCN / pentane
50-65%
R2
R1
Nuc
R3

(Eq. 2.12)

Nuc = $-CH(CO_2Me)_2$

119: $R^1 = R^2 = R^3 = H$
120: $R^1 = R^2 = H$, $R^3 = Me$
121: $R^1 = R^3 = Me$, $R^2 = H$
122: $R^1 = R^2 = Ph$, $R^3 = H$

Serendipitously, Dzwiniel also unearthed a more interesting alternative, involving the addition of excess maleic anhydride (Equation **2.13**); the mechanism for this transformation, as well as the fate of the cobalt in this process, has not been determined.


Co
H
Nuc
R
H
O
O
O
toluene, 55 °C
12 h
Cp2Fe+ PF6-
or air
Nuc
R

(Eq. 2.13)

Nuc = $-CH(CO_2Me)_2$

123: R = H, 92%
124: R = Me, 47%

A general method for cycloheptadiene decomplexation which is quantitative in the recovery of both the organic product as well as the cobalt template remains a goal of the work described in this dissertation.

Part C: Incorporation of Pro-Nucleophilic Functionalities in [3+2+2] Cycloadditions

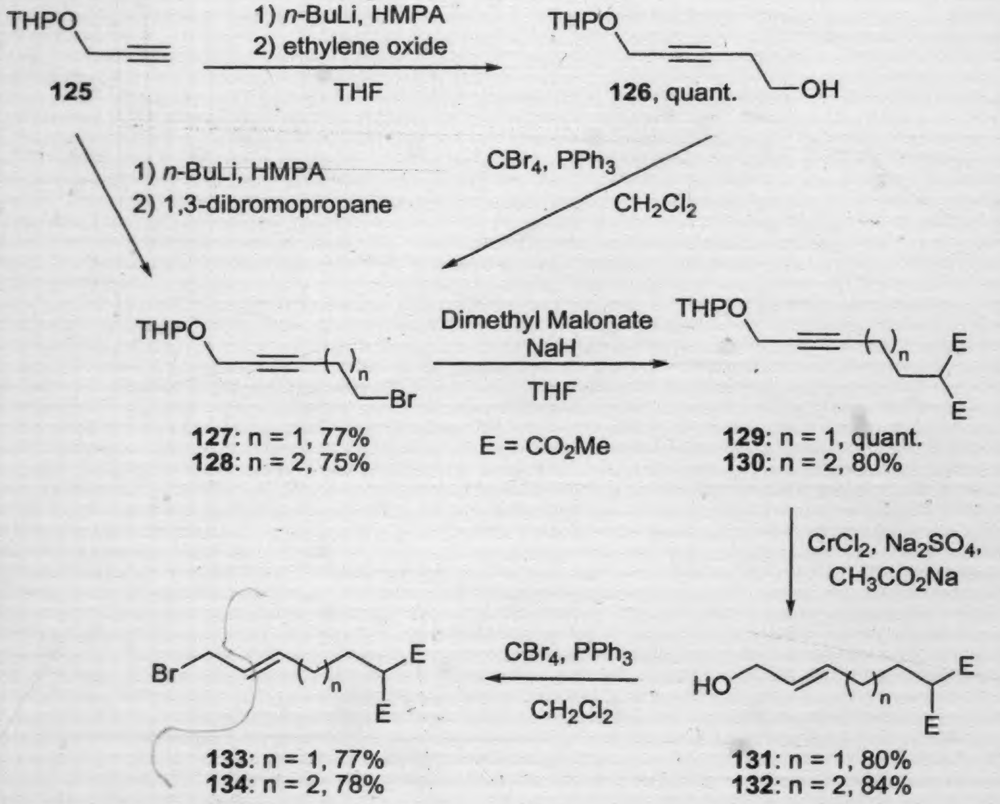
Although Dzwiniel expanded the scope of the [3+2+2] cycloadditions to include a number of substituted alkynes and allyl fragments bearing simple hydrocarbon groups, the tolerance of the cycloadditions for less chemically innocent functional groups was not investigated. Owing to the established regio- and stereoselectivity of the Co(III)-mediated [3+2+2] cycloaddition, the incorporation of more reactive functional groups into the cycloheptadienyl cycloadduct was an intriguing possibility as these functional groups could then be employed to further elaborate the seven-membered ring ligand.

Of specific interest was the incorporation of a pro-nucleophilic functional group, such as a malonate moiety, at a terminal position on the allyl fragment. In this manner, a tethered pro-nucleophile could be affixed to a Cp*Co(III) cycloheptadienyl [3+2+2] cycloadduct; this tether might subsequently be deprotonated and then undergo an intermolecular nucleophilic addition to the electrophilic cycloheptadienyl ligand and, in doing so, create a fused bicyclic system.

A preliminary investigation in this direction was undertaken by Endeshaw,[116] who synthesized the malonate-bearing allyl bromides **133** and **134** via a method developed by

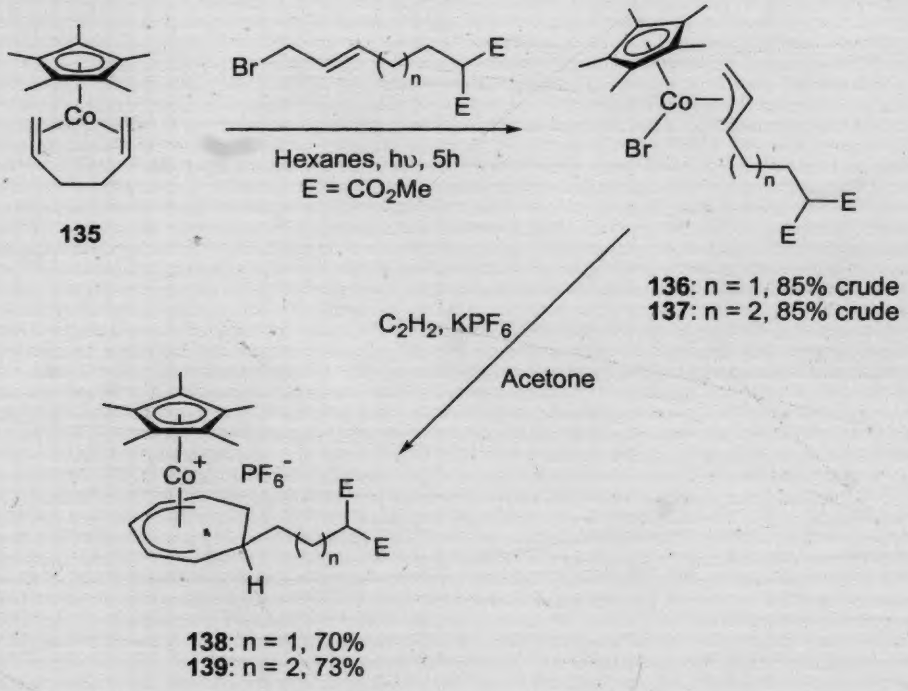
Deslongchamps.[117] By this route, both of the requisite allyl bromides **133** and **134** were accessed from THP-protected propargyl alcohol **125** in good overall yield (Scheme **2.14**).

Scheme 2.14

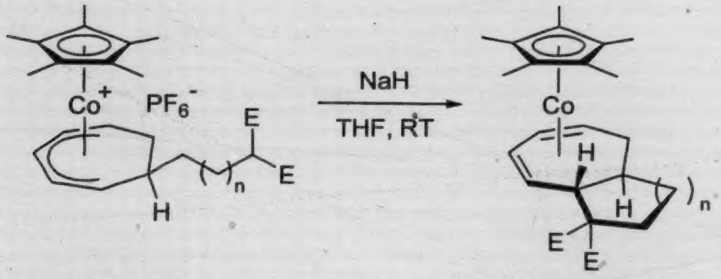

THPO
125
1) n-BuLi, HMPA
2) ethylene oxide
THF
THPO
OH
126, quant.
1) n-BuLi, HMPA
2) 1,3-dibromopropane
CBr4, PPh3
CH2Cl2
THPO
n
Br
127: n = 1, 77%
128: n = 2, 75%
Dimethyl Malonate
NaH
THF
E = CO2Me
THPO
n
E
E
129: n = 1, quant.
130: n = 2, 80%
CrCl2, Na2SO4,
CH3CO2Na
Br
n
E
E
133: n = 1, 77%
134: n = 2, 78%
CBr4, PPh3
CH2Cl2
HO
n
E
E
131: n = 1, 80%
132: n = 2, 84%

Endeshaw prepared the Cp*Co(III) allyl [3+2+2] substrates by photolytic oxidative addition of the allyl halides across the relatively robust Cp*Co(I) 1,5-hexadiene complex **135**, but the allyl complexes **136** and **137** thus obtained were not purified or characterized owing to their air-sensitivity. In the subsequent [3+2+2] cycloaddition step, however, these crude Cp*Co(III) allyl complexes furnished the desired cycloheptadienyl complexes **138** and **139** in good yield (Scheme **2.15**).

Scheme 2.15


Co
135
Br
E
n
E
Hexanes, hν, 5h
E = CO2Me
Co
Br
n
E
E
136: n = 1, 85% crude
137: n = 2, 85% crude
C2H2, KPF6
Acetone
Co+
PF6-
E
n
E
H
138: n = 1, 70%
139: n = 2, 73%

The intramolecular nucleophilic addition to furnish the fused bicyclic Cp*Co(I) cycloheptadiene complexes **140** and **141** was also accomplished by Endeshaw upon deprotonation of the malonate group under ambient conditions (Equation **2.14**). Endeshaw established the *trans* stereochemistry about the ring fusion by ^{1}H NMR spectroscopy as well as X-ray crystallography; the intramolecular cyclization proceeds with complete diastereoselectivity as nucleophilic attack occurs only at the face of the ring opposite from the metal.



138: n = 1
139: n = 2

140: n = 1, 71%
141: n = 2, 80%

(Eq 2.14)

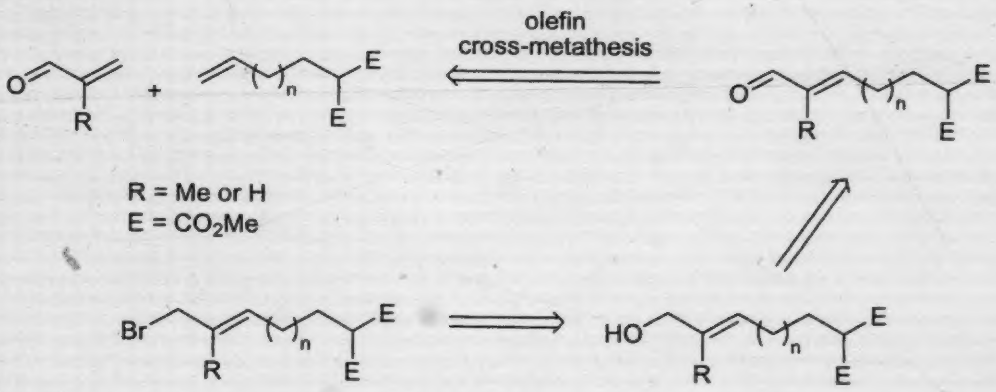
Part D: Project Goals

Although Endeshaw had demonstrated that fused bicyclic organic targets were accessible from intramolecular nucleophilic attack within [3+2+2] cycloadducts, there remained much work to be done. In particular, the analogous preparation of bicyclic organics possessing an angular methyl at a quaternary center was of interest, as this structural motif is known in a number of natural products[1-14] (*i.e.* Figure **1.1**).

Unfortunately, the route employed by Endeshaw to access the allyl bromides **136** and **137** was not suitable for the synthesis of the allyl bromide precursors, and a new route into these precursors was envisaged which made use of olefin cross-metathesis[118-122] technology developed in the last decade (Scheme **2.16**). Such methodology could also be harnessed as an alternative route to the known compounds **136** and **137**.

In addition to the preparation of seven-membered ring-containing bicyclic organic targets, another goal was specifically identified: despite advances made by Dzwiniel, a general method for the decomplexation in high yield of dienes from the Cp*Co(I) template remained an objective in the Stryker group.

Scheme 2.16

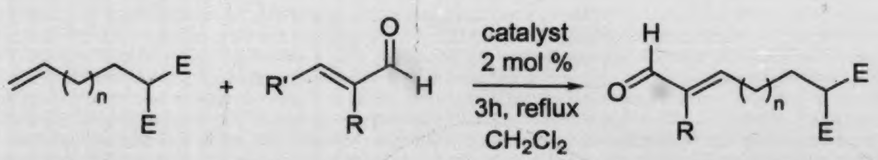

olefin
cross-metathesis
O
R
E
n
R = Me or H
E = CO_2Me
Br
HO

Section 2: Results and Discussion

*Part D: Synthesis of Cp*Co(III) Allyl Halides Bearing Latent Nucleophiles*

The two homologous ω-olefinic alkylmalonates **142** and **143** were prepared according to literature methods involving standard malonate alkylation conditions.[123,124] Unreacted dimethylmalonate as well as the unavoidable minor bis-alkylation product were removed chromatographically in accord with the published procedures.

Each of the four α,β-unsaturated aldehydes **146-149** were successfully prepared in high yield (Equation **2.15**) under mild cross-metathesis conditions in which the 2nd generation Grubb's catalyst **150** was employed. In principle, acrolein could have been employed as the electron deficient cross metathesis partner for the preparation of the aldehydes **146** and **147** but, despite being slightly less atom-economical, crotonaldehyde was used owing to the greater expense and difficulty of storage associated with acrolein.

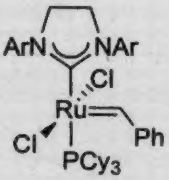


(Eq 2.15)

142: n = 1
143: n = 2
E = CO_2Me

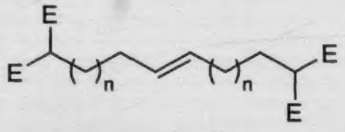
144: R = H, R' = Me
145: R = Me, R' = H

146: R = H, R' = Me, n = 1
147: R = H, R' = Me, n = 2
148: R = Me, R' = H, n = 1
149: R = Me, R' = H, n = 2
80-90%



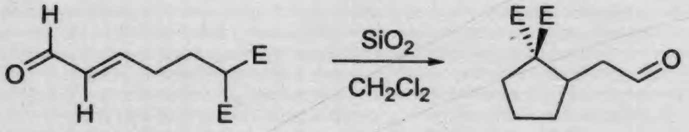
150: 2nd generation Grubbs' Catalyst
Ar = 2,4,6-trimethylbenzene

Although crude product was recovered from each cross-metathesis reaction in good yield (80-90%), none of the α,β-unsaturated aldehydes **146-149** were purified to analytical standards; the small but inevitable amounts (< 5%) of homodimer **151** or **152** which was present following work-up could not be completely removed chromatographically.



151: n = 1
152: n = 2
E = CO_2Me

In fact, efforts to purify substrate **147** by silica gel chromatography furnished the 5-membered ring compound **153**, presumably as a result of a cyclization process which was catalyzed by the weakly acidic stationary phase (Equation **2.16**). Fortunately, the subsequent reduction step was to furnish a product sufficiently different in polarity from the homodimer so as to permit chromatographic removal of this latter impurity.

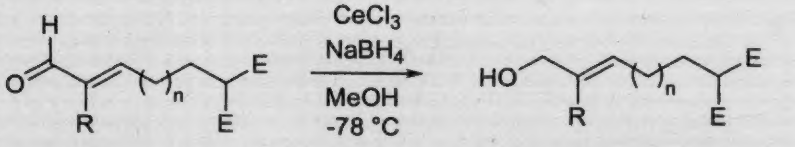


147 **153**

(Eq 2.16)

Although a number of methods have been reported for the 1,2-reduction of α,β-unsaturated ketones, fewer methods are widely used for the related 1,2-reduction of α,β-unsaturated aldehydes. DIBAL-H, normally the reductant of choice for this transformation, was not suitable for the reduction of compounds **146-149** owing to the presence of the ester functionalities. Instead, a Luche-type Ce(III)-mediated procedure[125] was employed, and the allyl alcohols **131**, **132**, **154**, and **155** were each isolated in moderate yield (Equation **2.17**). In each case, silica gel chromatography effectively removed any homodimer **151** or **152** remaining from the prior cross-metathesis step.

In each case, the regioselectivity of the reduction was reasonably high. However, a small amount of conjugate reduction product formed in each case (~5%) could not be removed chromatographically and was therefore carried on as an impurity in the subsequent bromination step. The yields given in Equation **2.17** are 2-step yields based on the amount of olefin **142** or **143** used in the previous cross-metathesis step.



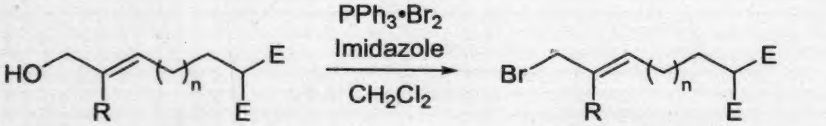
(Eq 2.17)

146-149

E = CO_2Me

131: R = H, n = 1, 61%
132: R = H, n = 2, 55%
154: R = Me, n = 1, 53%
155: R = Me, n = 2, 57%

The alcohol functionality was then converted to the corresponding allyl bromide via a standard triphenylphosphine methodology (Equation **2.18**). The triphenylphosphine bromine adduct was prepared *in situ* prior to alcohol addition, and imidazole was employed as a proton scavenger. In each case, yields of allyl bromide were moderate. As before, a small amount (< 5%) of saturated analogue was present in each



(Eq 2.18)

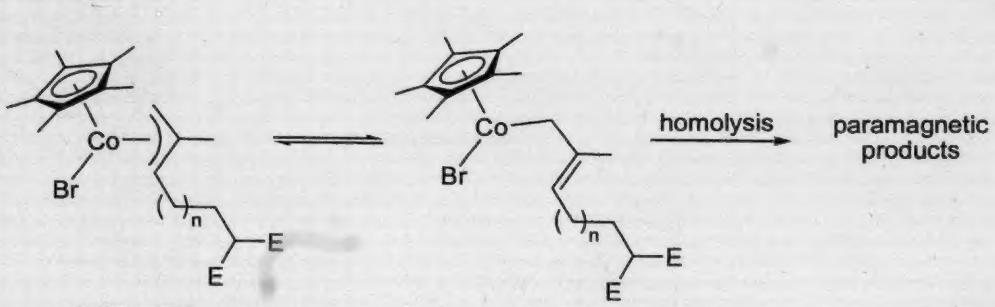
131, 132, 154, or 155

133: R = H, n = 1, 74%
134: R = H, n = 2, 75%
156: R = Me, n = 1, 69%
157: R = Me, n = 2, 70%

case, owing to the incomplete regioselectivity of the prior reduction step. Again, efforts to remove this impurity chromatographically from each allyl bromide were fruitless. Fortunately, the saturated halides were not expected to interfere with subsequent oxidative addition steps and could therefore simply be removed at a later juncture. In this respect, however, the more classical pathway employed by Endeshaw for the preparation of **133** and **134** was superior as the saturated bromides were absent from his products.

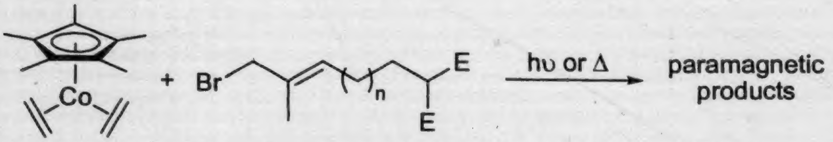
Since Endeshaw had previously prepared non-methylated Cp*Co(III) allyl compounds **136** and **137** from the Cp*Co(1,5-hexadiene) **135** (Scheme **2.15**), the same photolytic conditions were assayed for the analogous preparation of the methylated complexes **158** and **159**. Disappointingly, however, these efforts furnished only a blue/green solution of unidentified paramagnetic material. It is quite likely that the oxidative addition did proceed as desired from **135** to furnish allyl complexes **158** and **159**. However, the methyl substituent at the central allyl carbon likely renders the allyl ligand more prone to adopting an η^1-configuration. Under the harsh photolytic conditions employed, it is not surprising that bond homolysis would ensue from **158** and **159** to generate Co(II) decomposition products (Scheme **2.16**).

Scheme 2.16


Co
Br
n
E
E
Co
Br
n
E
E
homolysis
paramagnetic products

158 or 159

Similarly, photochemical conditions failed to furnish Cp*Co(III) allyl complexes from Cp*Co(I) bis(ethylene) **43** (Equation **2.19**); again, only blue-green paramagnetic material was obtained. Likewise, gentle heating of the reaction mixture in the dark was unproductive.

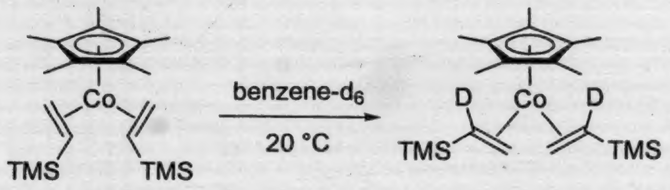

Co
+
Br
n
E
E
hυ or Δ
paramagnetic products

(Eq 2.19)

43 **156 or 157**

At room temperature, the thermal oxidative addition of bis(ethylene) complex **43** was more promising, although still unsatisfactory. The product mixture recovered from these attempts also contained some paramagnetic material, as evidenced by colour and by broadness in the ^{1}H NMR spectrum. As well, a significant amount of an unidentified impurity was also present. However, Cp*Co(III) allyl complexes could be identified as major components of the mixtures. Interestingly, Cp*Co(I) starting material **43** was also a major component of the product mixture, whereas the organic allyl halide **156** or **157** (which had been employed in slight excess) was absent.

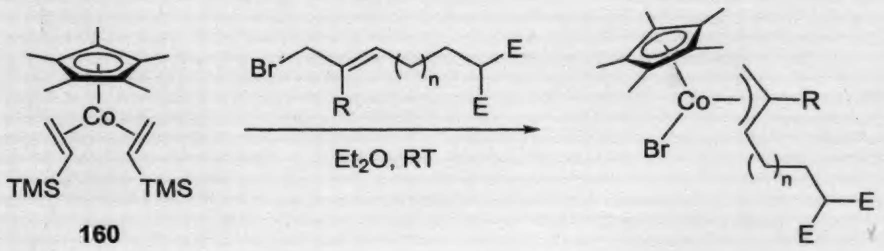
It was therefore necessary to identify reaction conditions which would increase the rate of oxidative addition relative to the rate of decomposition and by-product formation. As such, a more labile source of half-sandwich Cp*Co was sought. Brookhart had previously reported[126-128] the preparation and chemistry of the Cp*Co(I) bis(vinyltrimethylsilane) complex **160**. In particular, the vinyltrimethylsilane ligand was found to be considerably more thermally labile in solution than ethylene; Brookhart quantitatively measured these rates of dissociation as part of a study of the rate of H/D exchange with deuterated benzene (Equation **2.20**).[127]



160 **160-d_2**

(Eq 2.20)

Gratifyingly, the oxidative additions of both **156** and **157** to Cp*Co(I) complex **160** proceeded quite rapidly at room temperature; in each case, reaction appeared to be complete within several minutes as evidenced by complete disappearance of the brick red colour of **160** and the emergence of the very deep purple colour characteristic of Cp*Co(III) allyl complexes (Equation **2.21**).



160

(Eq 2.21)

136: R = H, n = 1
137: R = H, n = 2
158: R = Me, n = 1
159: R = Me, n = 2

In an effort to optimize the formation of allyl complexes **136**, **137**, **158**, and **159**, a range of reaction conditions were assayed. Diethyl ether and benzene were identified as two suitable organic solvents, whereas dichloromethane, acetone, and THF among others failed to furnish clean Co(III) allyl products. It is not surprising that the later two solvents were unsuitable for the oxidative addition, as the coordinating nature of these solvents would promote isomerization of **158** or **159** (if formed) to the η^1-isomer and thus accelerate homolytic decomposition. Performing the addition with strict exclusion of light also failed to have a discernible effect on product formation.

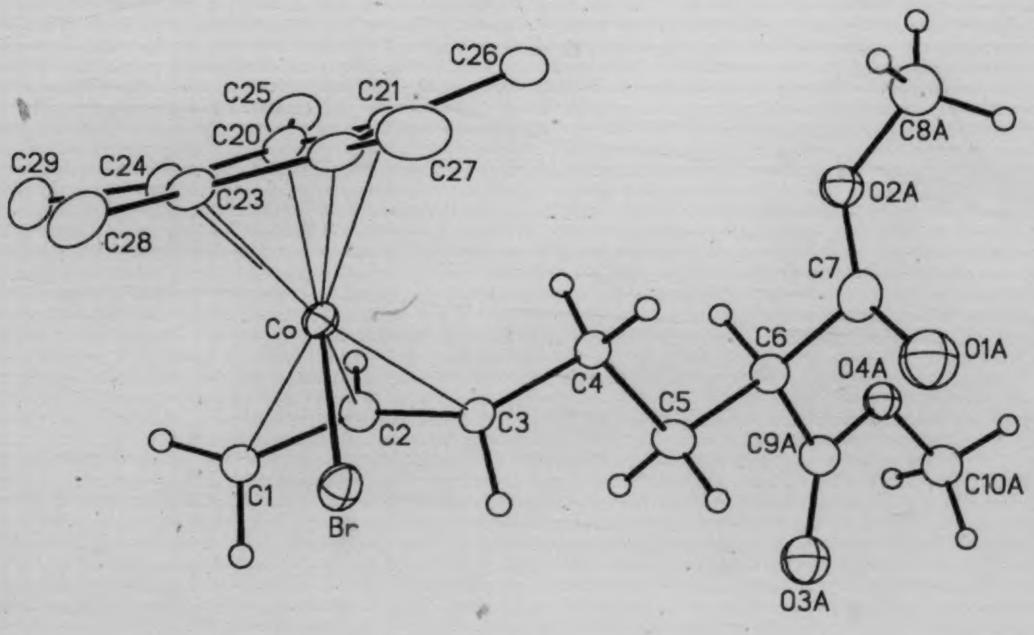
In any event, attempts to purify the methylated allyl complexes **158** and **159** were hindered owing to the high thermal sensitivity of these compounds. Even in the glovebox, repeated handling of **158** and **159** in solution at room temperature gave rise to a paramagnetic blue green precipitate. It is noteworthy that Dzwiniel also reported significant thermal instability for 1,2-disubstituted allyl complexes; some of these compounds were so resistant to purification that Dzwiniel prepared them immediately prior to use and employed them in [3+2+2] chemistry without purification. As previously stated, this propensity for decomposition is likely due to a more accessible η^1 configuration, owing to the presence of substituents at two of the three allyl positions.

The NMR characterization of allyl complexes **158** and **159** was also complicated by this tendency towards decomposition. Even after filtration and crystallization from pentane, significant broadening was observed in the ^{1}H NMR spectra of **158** and **159**. The yields listed in Equation **2.21** represent those after a single crystallization from ether/pentane; crude yields approached 90% in all cases. The yields of non-methylated complexes **136** and **137** are somewhat lower than those reported by Endeshaw from the oxidation of Cp*Co(I) 1,5-hexadiene, although the allyl complexes isolated by Endeshaw did contain significant levels of paramagnetic impurity.

A low-temperature NOESY experiment was performed on methylated allyl complex **158** to confirm the solution-state stereochemistry of the allyl fragment; the presence of a central-carbon substituent precluded the straightforward use of coupling constants to establish the *syn* configuration, although chemical shift data were consistent with this stereochemistry. The detection of a NOE interaction between the Cp* protons and the methyl protons at the central carbon of the allyl carbon indicated an *exo* allyl ligand configuration, as is typical of most other known Cp*Co(III) allyl complexes.

This stereochemical assignment was reinforced by X-ray crystallographic analysis of the non-methylated complex **137**. Despite the difficulties in obtaining pure Cp*Co(III) allyl complexes **136**, **137**, **158**, and **159** to the exclusion of paramagnetic material, a small amount of X-ray quality crystals of **137** were obtained from slow crystallization from ether/pentane in the glovebox at -34 °C. Of the four allyl complexes **136**, **137**, **158**, and **159**, **137** is the only one for which crystallographic data has been obtained.

Figure 2.1: ORTEP for Complex **137** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0404


C26
C25
C21
C20
C29
C24
C23
C27
C28
Co
C1
Br
C2
C3
C4
C5
C6
C7
C8A
O2A
O1A
O4A
C9A
C10A
O3A

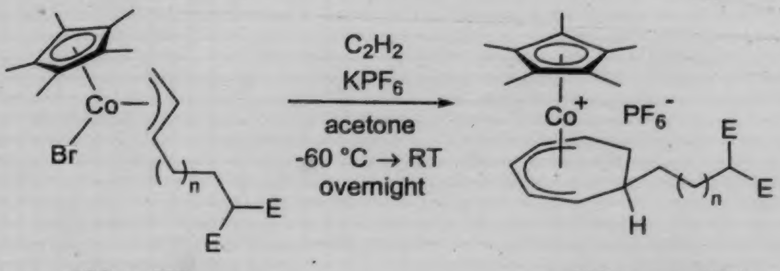
Final Residuals: $R_1 = 0.0563$; $wR_2 = 0.1553$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C2, 1.426(7); C2-C3, 1.399(7); Co-C1, 2.085(6); Co-C2, 2.013(5); Co-C3, 2.125(5).

The dihedral angle between the planes defined by C20-C24 and C1-C3 = 14.3(5)°.

Part E: Synthesis of Bicyclic Organic Compounds via [3+2+2] Cycloaddition

With the requisite allyl complexes in hand, an effort was made to effect clean [3+2+2] cycloaddition reactions with acetylene. Endeshaw had previously prepared cyclopentadienyl complexes **138** and **139** in acetone, using KPF_6 exchange to remove the inner-sphere halide ion by precipation (Equation **2.22**); this strategy had been previously employed by Dzwiniel (*vide supra*). More recent efforts by the current author to improve the yields of **138** and **139** by using silver ion to abstract the bromide did not meet with an improvement in yield; to date, Endeshaw's original cycloaddition conditions remain optimal. Owing to the difficulties associated with isolating and purifying the intermediate allyl complexes **136** and **137**, Endeshaw's optimal procedure uses these complexes in the crude, unpurified form immediately after formation by oxidative addition.

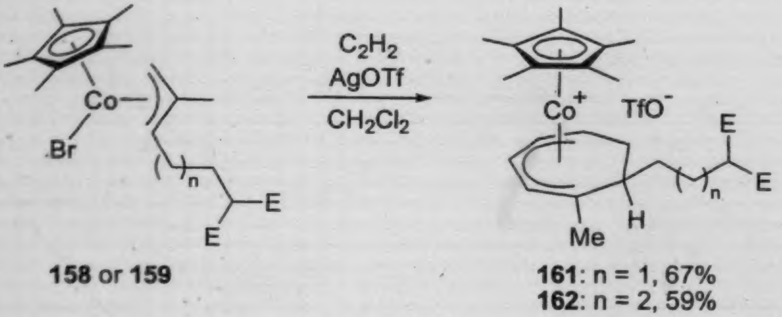


(Eq 2.22)

136 or **137**

138: n = 1, 70%
139: n = 2, 73%

On the other hand, the use of KPF_6 in acetone failed to yield any tractable material from methylated analogues **158** and **159** in the presence of acetylene. Ultimately, the optimal conditions for these transformations were identified; silver ion was necessary for *in situ* halide ion abstraction from **158** and **159** at low temperature. A great deal of effort was expended in optimizing the conditions for the [3+2+2] preparations of the methylated analogues **161** and **162**. Unfortunately, no conditions could be identified that furnished these cycloheptadienyl complexes cleanly and in high yield. The best yields of cycloadducts **161** and **162** were moderate at best (Equation **2.23**): the yields listed are of products which contain a significant level of an unidentified impurity (*vide infra*). It is noteworthy that the low yields were not improved after repeated attempts to purify the starting allyl complexes and, thus, the optimal procedure employs these Co(III) allyl complexes in a semi-crude form after a single crystallization from ether/pentane.



(Eq 2.23)

Even the most optimal cycloadditions of **158** and **159** were plagued by the formation of significant brown-green unidentified material which contained some paramagnetic compounds, as evidenced by broadness in the ^{1}H NMR spectra. The formation of such material is not uncommon in the [3+2+2] cycloaddition; Dzwiniel also observed minor but varying amounts of such a contaminant in the majority of his cycloaddition efforts. In the case of compounds **161** and **162**, efforts to remove this impurity were nearly fruitless; although the purity of the products improved slightly with column chromatography, the contaminants co-elute with the cycloheptadienyl products under any of the chromatographic conditions employed. As a result, the cycloheptadienyl complexes were carried on in an impure form in the synthetic sequence; fortunately, the subsequent synthetic step was to markedly change the polarity and oxidation state of the seven-membered ring-containing organometallic complex; thus, removal of the uncharacterized [3+2+2] byproducts was ultimately accomplished. For the purposes of using the cleanest possible Cp*Co(III) cycloheptadienyl substrates **161** and **162** in evaluating subsequent base-promoted cyclization reactions, the most pure (by NMR determination) fractions of [3+2+2] cycloadduct were those that eluted last from column chromatography. Unfortunately, only a small fraction of the total cycloadduct could be recovered in this improved state of purity and, despite this, analytically pure material was not recovered.

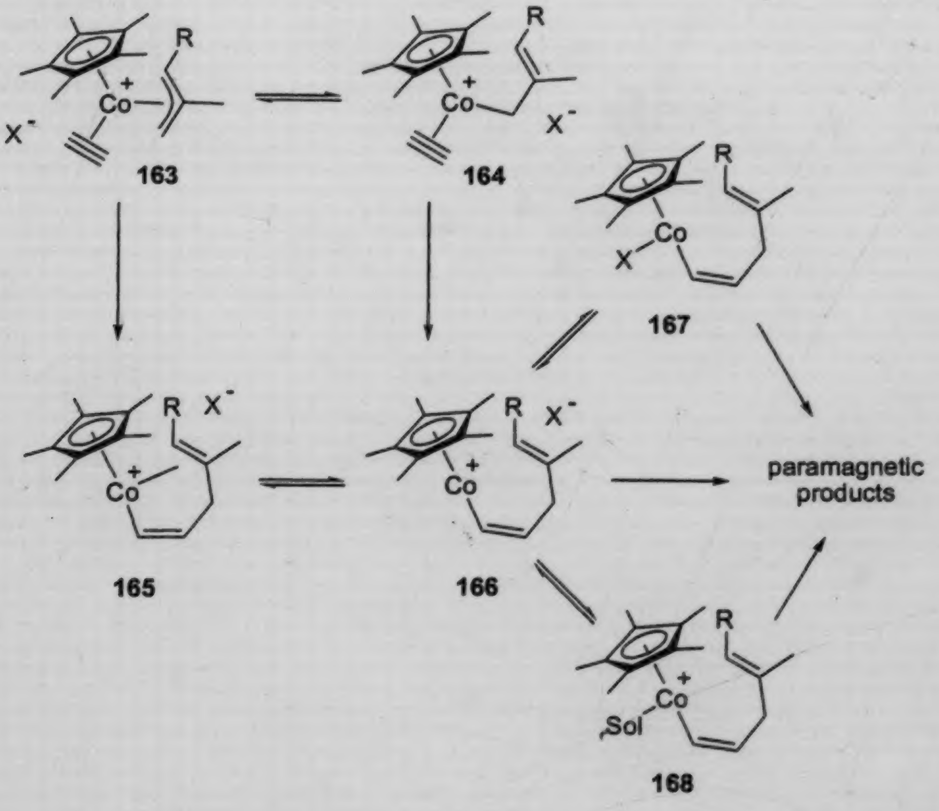
The failure of the methylated analogues **158** and **159** to efficiently undergo the [3+2+2] cycloaddition reaction must be in some way a result of the central-carbon substituent, as the otherwise identical complexes **136** and **137** were far more productive in reaction with acetylene. This methyl substituent had previously been shown to render the Cp*Co(III) allyl complex far less thermally and photochemically stable presumably due to a more accessible η^1-allyl configuration (*vide supra*, Scheme **2.16**); decomposition of the allyl complexes **158** and **159** under [3+2+2] conditions might also be occurring in competition with the cycloaddition, thus lowering the yield of cycloheptadienyl complexes.

In addition, there are other possible pathways through which the methyl substituent might divert the reaction pathway from the desired route. It is plausible that the initial migratory insertion step (as per Scheme **2.11**) is hindered by the presence of this substituent; indeed, a central-carbon substituent would be expected to exert a subtle influence on the ground-state binding of the allyl fragment which could ultimately hinder an eventual migratory insertion. If the assumption is made that the central-carbon methyl group acts to weaken the carbon-metal bond at this position and thus lower the energy barrier to the η^1-allyl configuration, it stands to reason that the migratory insertion will occur such that the alkyne inserts at the less hindered terminus of the allyl fragment. Indeed, Dzwiniel has speculated that this insertion might actually *require* the allyl to be in an η^1-configuration. That being the case, the vinyl-olefin intermediate **165** would form from **166** only after re-coordination of the pendant olefin (Scheme **2.17**). If this re-coordination is sterically hindered, homolytic decomposition (perhaps after halide or solvent coordination) will compete with cycloaddition.

Interestingly, the methyl substituent could at this point actually prove beneficial to the desired [3+2+2] process, as it might reasonably be expected to inhibit five-membered ring formation from vinyl olefin intermediate **165**; this undesired annulation is one of the most problematic obstacles to seven-membered ring formation (Schemes **2.11** and **2.12**). On the other hand, the substituent would also increase the lability of the olefin fragment and thus facilitate a homolytic decomposition pathway via an η^1-vinyl complex such as **166**, **167**, or **168**.

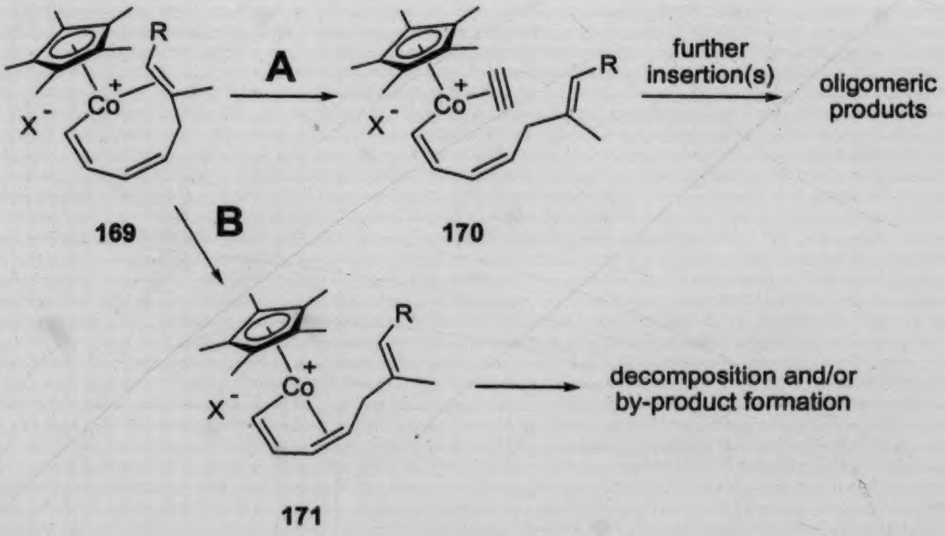
If a second alkyne successfully coordinates to the metal and subsequently inserts into the metal-vinyl bond, yet another possibility exists for potential diversion of the reaction pathway from the typical [3+2+2] route (Scheme **2.18**). In the final carbon-carbon bond-forming event, the newly-formed vinyl group must migrate to the substituted end of the olefin fragment. Again, the methyl substituent may retard this process as a result of steric influence. However, it is also likely that the effect of the methyl group is more subtle, altering the geometry in which the olefin group coordinates to the cobalt and therefore altering the geometry of any subsequent insertion. Indeed, the methyl group may hinder olefin coordination altogether, leading to a subsequent coordination and insertion of further alkyne fragments, leading to oligimerization (pathway A, Scheme **2.18**) or to other unidentified by-products (pathway B).

Scheme 2.17

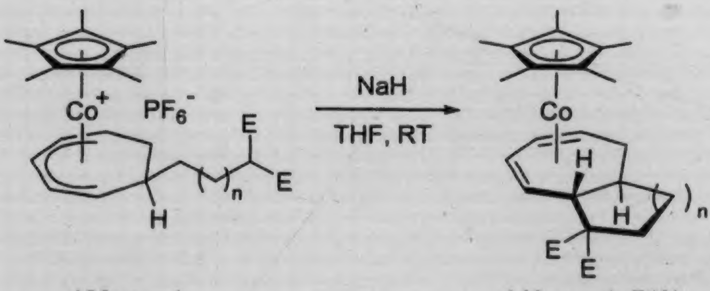

R
+
Co
X⁻
163
R
+
Co
X⁻
164
R
Co
X
167
R X⁻
+
Co
165
R X⁻
+
Co
166
paramagnetic products
R
+
Co
Sol
168

Regardless of the exact mechanism(s) by which the methyl substituent exerts an influence, it is clear that even this small (and seemingly subtle) structural change has a profound influence on the [3+2+2] cycloaddition. It may be that an entirely new metal template will need to be developed and employed for the cycloaddition of more heavily substituted allyl complexes analogous to **158** and **159**; the development of more "ideal" organometallic templates for this process remains an important goal in the Stryker group.

Scheme 2.18



Although yields of cycloheptadienyl complexes **161** and **162** were modest and the complexes could not be isolated in high purity, the subsequent base-promoted cyclization step was nonetheless investigated. Endeshaw had previously prepared the bicyclic organometallic targets **140** and **141** via an intramolecular nucleophilic attack promoted by sodium hydride (Equation **2.24**). As part of the current study, sodium hydride was also found to be productive in the cyclization of methylated analogue **161** to furnish bicyclic complex **172**, albeit in low (37%) yield.

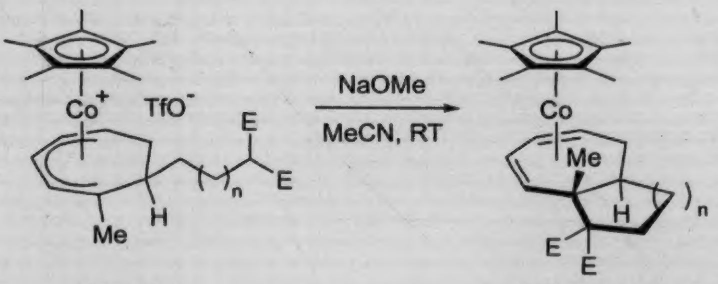


(Eq 2.24)

138: n = 1
139: n = 2

140: n = 1, 71%
141: n = 2, 80%

More effective, however, was the use of of sodium methoxide suspended in acetonitrile (Equation **2.25**). Under these cyclization conditions, the Cp*Co(I) bicyclic organometallic targets **172** and **173** could be obtained from the Co(III) precursors in high yield. Purification of the Cp*Co(I) complexes was effected by passage through deactivated (activity IV) alumina, followed by crystallization from pentane at low temperature. Notably, the complexes **172** and **173** had a much lower solubility in pentane than many other similar Cp*Co(I) dienes that have been purified in this manner, resulting in a very efficient recovery of **172** and **173** from the crystallizations.



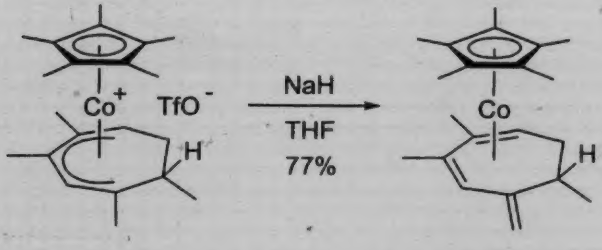
161: n = 1
162: n = 2

172: n = 1, 80%
173: n = 2, 71%

(Eq 2.25)

Whereas Endeshaw was able to employ ^{1}H-^{1}H coupling constants to support the *trans* stereochemistry at the nascent ring fusion in complexes **140** and **141**, no such analysis was possible for analogues **172** and **173**, owing to the methyl substituent at the bridgehead position. Although a *trans* geometry for **172** and **173** could be implied by comparison of the other ^{1}H NMR signals in the complexes with those of the unmethylated cases, confirmation of the *trans* geometry was achieved by X-ray crystallographic analysis of **173** (Figure **2.2**).

It is also notable that no exocyclic methylene Cp*Co(I) complexes were formed as a result of competitive deprotonation allylic to the coordinated fragment. Prior to this investigation, Etkin had noted that treatment of complex **51** with sodium hydride resulted in clean deprotonation to form an exocyclic methylene compound (Equation **2.26**).

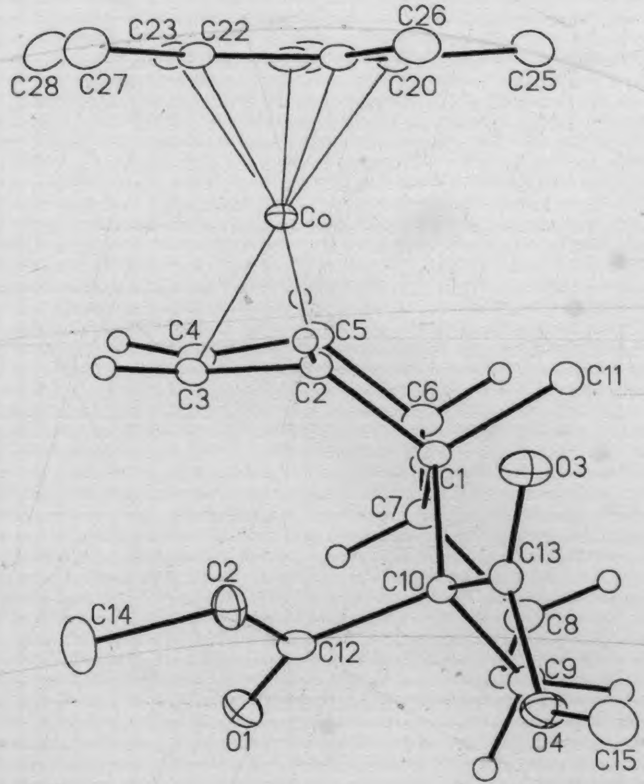


51

174

(Eq 2.26)

Figure 2.2: ORTEP for Complex **173** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0312


C23
C22
C26
C28
C27
C20
C25
Co
C4
C5
C3
C2
C6
C11
C1
O3
C7
C13
O2
C10
C14
C8
C12
C9
O1
O4
C15

Final Residuals: $R_1 = 0.0407$; $wR_2 = 0.1045$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

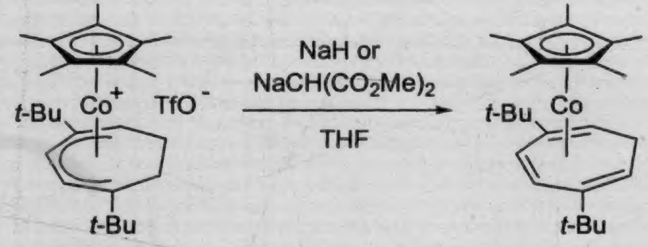
Selected Bond Distances (Å): C1-C2, 1.426(7); C2-C3, 1.399(7); Co-C1, 2.085(6); Co-C2, 2.013(5); Co-C3, 2.125(5).

The dihedral angle between the planes defined by C20-C24 and C2-C5 = 7.85(6)°.

The dihedral angle between the planes defined by C2-C5 and C1, C2, C5 & C6 = 45.00(10)°.

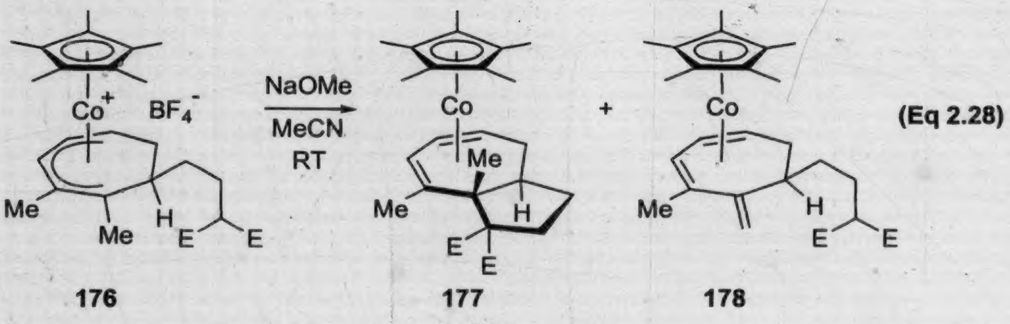
The dihedral angle between the planes defined by C1, C2, C5 & C6 and C1, C6, C7 & C10 = 53.22(10)°.

As well, Dzwiniel observed endocyclic deprotonation reactions instead of nucleophilic additions to some cycloheptadienyl complexes, although in these cases the sterically substantial *tert*-butyl substituent impeded the approach of nucleophile (Equation **2.27**). Nonetheless, the nucleophilic formation of the adjacent quaternary centers in complexes **172** and **173** was by no means a foregone conclusion.



63 **175** **(Eq 2.27)**

It has since become apparent that those factors responsible for the partition between intramolecular nucleophilic attack and exocyclic methylene formation are quite subtle. Recently, Ylijoki in the Stryker group prepared the analogous 1,2-dimethyl Cp*Co(III) cycloheptadienyl complex via a novel [5+2] cycloaddition pathway which was unearthed by the present author (Chapter 4 of this thesis); attempts to form the bicyclic Cp*Co(I) compound **177** from **176** by nucleophilic cyclization were plagued by competitive formation of the exocyclic methylene complex **178** (Equation **2.28**). The desired product **177** constituted about 65% of the total isolated Co(I) product from **176**. The relative amount of **177** dropped to approximately 20% upon gentle heating, indicating that the exocyclic methylene product **178** is, in fact, thermodynamically preferred.



(Eq 2.28)

Part F: Oxidative Decomplexation of Bicyclic Organic Products

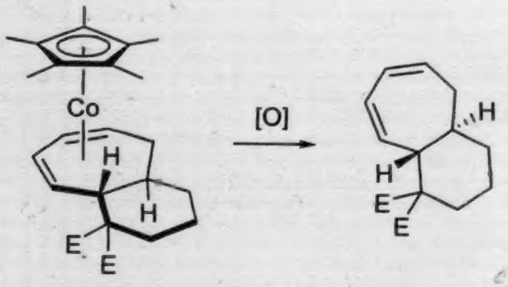
A method for the clean, near-quantitative removal of seven-membered ring products from the Co(I) template had not been fully realized. Thus, an investigation towards this goal was undertaken, initially in collaboration with Endeshaw. Dzwiniel had previously identified several oxidative methods for product decomplexation (*vide supra*) which furnished organic product in moderate yield; one major difficulty identified by Dzwiniel was the propensity for many of the standard oxidizing agents to react not only with the Co(I) template (as desired), but also with the decomplexed organic product after the fact.

As the [3+2+2] cycloaddition process is stoichiometric with respect to cobalt, the ideal decomplexation method would not only be quantitative with respect to organic product recovery, but also with respect to the recovery of the metal template in some potentially useful form; despite its ubiquitous nature, Cp* is expensive to purchase and onerous to synthesize.

Because the Cp*Co(III) allyl complexes required for cycloaddition had been prepared photolytically by reaction of organic allyl halides with Cp*Co(I) *non-*

conjugated diene complexes, the potential utility of organic halides for the decomplexation of *conjugated* cycloheptadiene complexes was thus considered. Although there were no known examples of the oxidative addition of an allyl halide to a Cp*Co(I) conjugated diene complex, Endeshaw successfully displaced the normally robust non-conjugated 1,5-hexadiene ligand by photolysis in the presence of allylic halide **133** or **134** (Scheme **2.15**). If such an allyl halide-promoted decomplexation could be realized, the Cp*Co template might be recovered as a Cp*Co(III) allyl halide complex suitable for use in another [3+2+2] cycloaddition.

To this end, Endeshaw evaluated the oxidative methods previously employed by Dzwiniel in comparison to the photolytic oxidation in the presence of allyl bromide (Equation **2.29**).



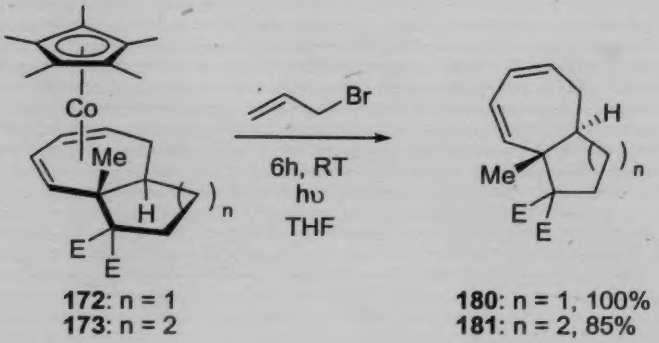
141 **179**

(Eq 2.29)

Conditions	Yield
$CpFe^+ PF_6^-$, MeCN/pentane from -78 °C to RT	43%
Maleic anhydride (5 eq.), toluene at 55 °C, 12h	70%
Allyl bromide, hexane hν	80%

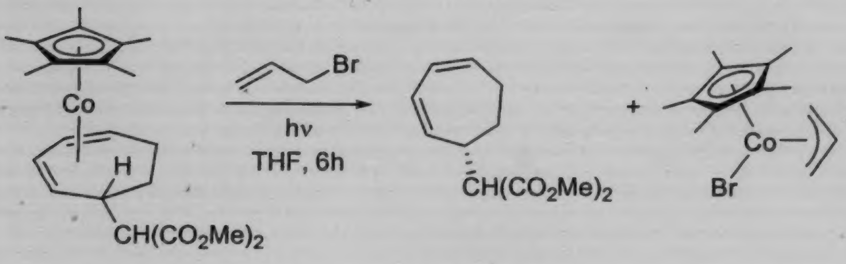
Gratifyingly, this new photolytic method furnished clean decomplexed organic cycloadduct in high yields, although Endeshaw did not undertake to recover the metal template in any of these preliminary runs.

The present author investigated the decomplexation of methylated complexes **172** and **173**; in each case, the photolytic decomplexation in THF with an excess of allyl bromide furnished clean organic product in high yield after chromatography (Equation **2.30**). The colour of the reaction solution changed from the deep ruby-red characteristic of Co(I) diene complexes to a light blue-green solution more characteristic of Co(II) or Co(III); the Co template was not recovered from any of these runs. THF was employed as solvent instead of hexane as the blue-green organometallic by-product is insoluble in the hydrocarbon and thus formed a crust on the inner surface of the glassware, potentially inhibiting complete reaction.



(Eq 2.30)

In an effort to optimize the photolysis conditions for the recovery of both the organic product as well as the metal template, the model Cp*Co(I) cycloheptadiene template **182** was employed. Whereas decomplexation of this species with excess allyl bromide also furnished the organocobalt template in an unidentified blue-green form, the use of a single equivalent of allyl bromide resulted in the formation of a deep purple solution typical of Cp*Co(III) allyl halides (Equation **2.31**). Upon removal of the THF solvent, the crude mixture was dissolved in a small amount of pentane; purple precipitate formed at this stage and filtration allowed for the separation of the soluble organic product **183** from the insoluble Cp*Co(III) allyl bromide **184**. In this manner, both the organic seven-membered ring product and the organometallic template were recovered cleanly and in good yield.



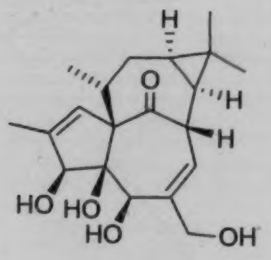
(Eq 2.31)

182 **183**, 83% **184**, 61%

Despite this promising result, much work in this area remains to be done. Although allyl bromide promotes clean decomplexation and recovery of the Co template, it is not clear if substituted allyl bromide compounds will be equally productive. Indeed, the instability of the central-carbon substituted Cp*Co(III) allyl complexes **158** and **159** indicate that such a method will not be general for all organic allyl halides. As well, the difference in colour between the Cp*Co(I) dienes and the Cp*Co(III) allyl halide products raises the possibility that a wavelength filter might be employed to permit photochemical oxidative decomplexation while excluding wavelengths that promote decomposition of the Cp*Co(III) allyl halide product.

Part G: Cobalt Mediated [3+2+2] Cycloadditions as a Route to "Inside-Outside" Stereochemistry

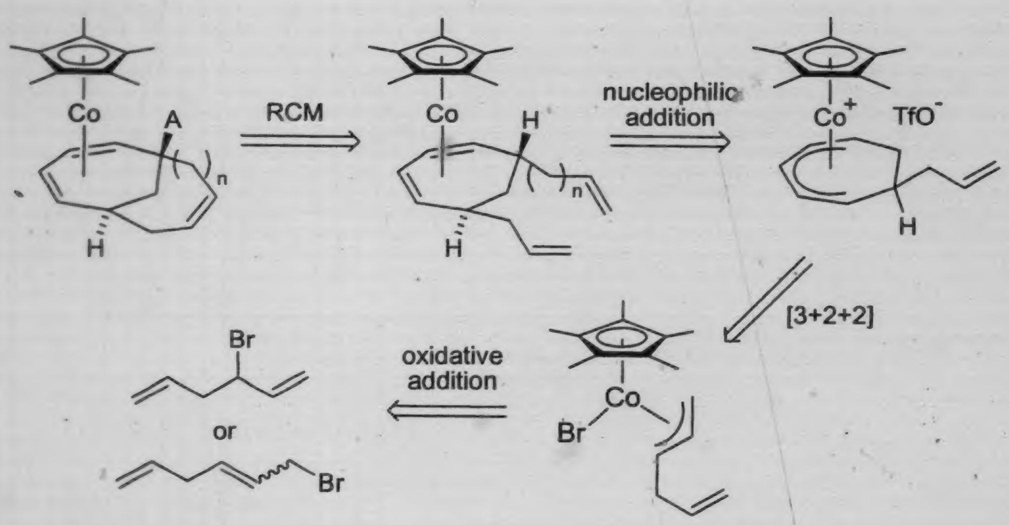
The [3+2+2] cycloaddition was also investigated as a prospective basis for the preparation of large bicyclic seven-membered ring compounds exhibiting the unusual "inside-outside" stereochemistry at the bridgehead positions.[129] Perhaps the most notable natural product of this sort which has been assailed synthetically in recent years is ingenol.[130-137] Despite these breakthroughs, the synthesis of targets possessing the unusual "inside-outside" stereochemistry remains a modern synthetic challenge, as no general methods exist for the assembly of this motif.



Ingenol

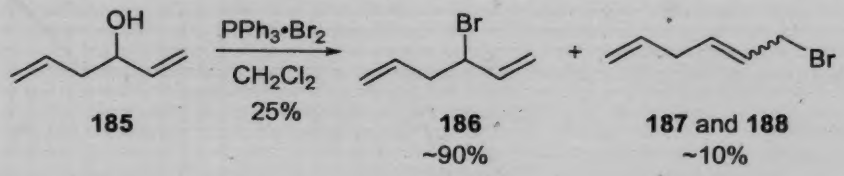
Our synthetic strategy for the realization of this goal relies on olefin ring-closing metathesis for the crucial cyclization event (Scheme **2.19**). The requisite olefin functionalities could in principle be installed in a 1,3-*trans* relative stereochemistry,

Scheme 2.19



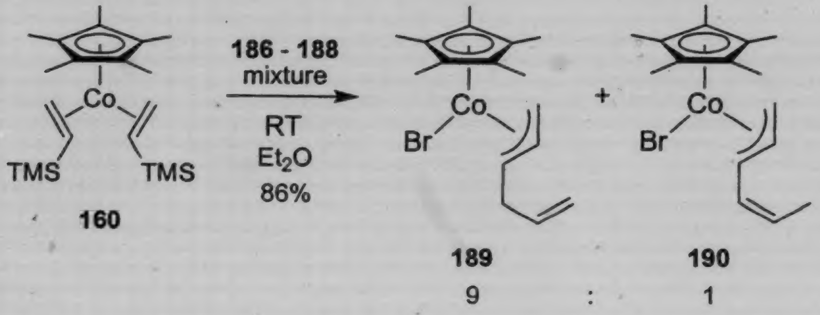
by harnessing the established regio- and stereoselectivity of the [3+2+2] cycloaddition reaction and intermolecular nucleophilic alkylation. One olefin functionality would thus be installed prior to the cycloaddition, while the other would be installed following the cycloaddition.

To probe the actual reactivity, commercially available 1,5-hexadiene-3-ol **185** was converted to the bromide using the triphenylphosphine-bromine adduct (Equation **2.32**). Although the direct substitution compound **186** was the major product, the rearranged *E*- and *Z*- primary bromides **187** and **188** were also present in small amounts. As all three of the allyl bromides **186 - 188** should render the same Cp*Co(III) allyl bromide upon oxidative addition, the allyl bromides were employed as a mixture.


OH
PPh3•Br2
CH2Cl2
25%
Br
+
Br
185
186
~90%
187 and 188
~10%

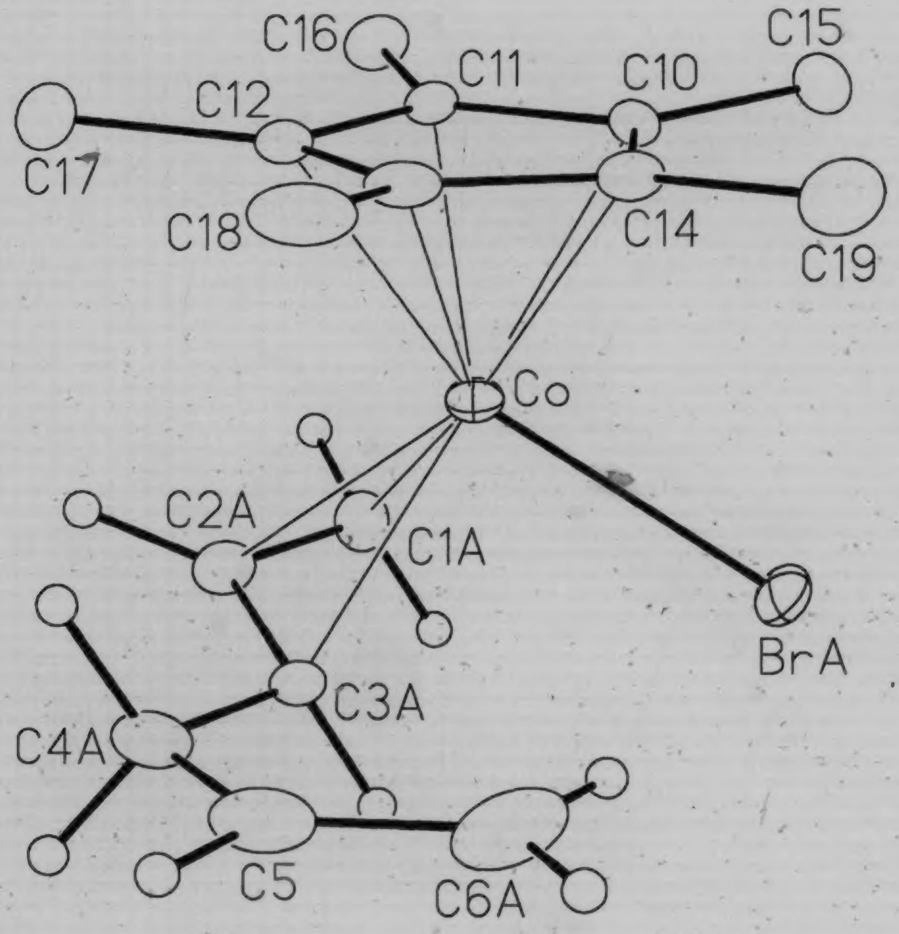
(Eq 2.32)

The oxidative addition of the halides **186 - 188** was effected in high yield by addition of the halide mixture at room temperature to a solution of bis(vinylsilane) complex **160** in ether (Equation **2.33**). A small amount of the isomerized complex **190** was evident in the product mixture, and could not be removed by crystallization. Although crystals of **189** suitable for X-ray diffraction studies (Figure **2.3**) were grown at low temperature from a mixture of pentane and diethyl ether, NMR analysis of these crystals revealed that **190** was still present and the relative amount of **190** was unaffected by the crystallization. The structure of **190** differs from that of **189** only in the placement of the double bond. It is therefore not surprising that **190** was not excluded from **189** during crystal formation and, apparently does not prevent convergence of the crystallographic structure solution.


Co
TMS
TMS
160
186 - 188
mixture
RT
Et2O
86%
Co
Br
+
Co
Br
189
190
9
:
1

(Eq 2.33)

Figure 2.3: ORTEP for Complex **189** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0344


C16
C11
C10
C15
C12
C17
C18
C14
C19
Co
C2A
C1A
BrA
C3A
C4A
C5
C6A

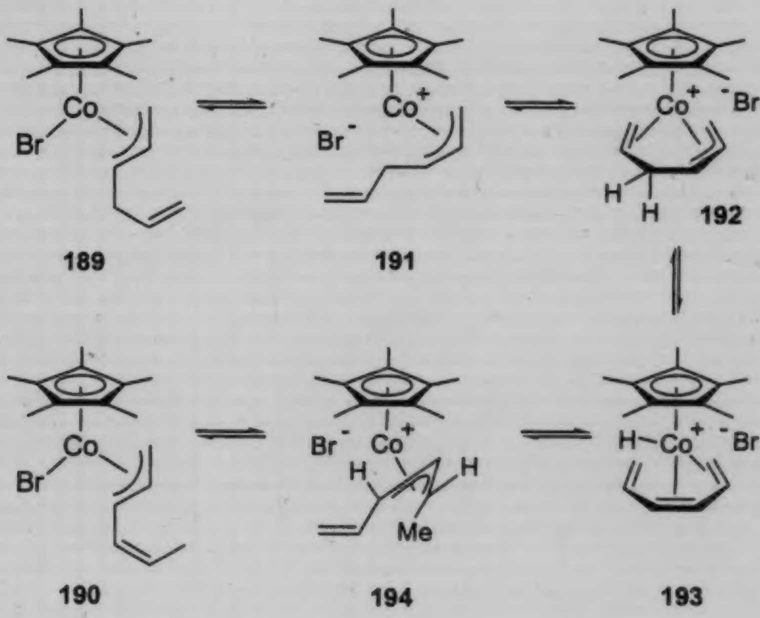
Final Residuals: $R_1 = 0.0524$; $wR_2 = 0.1422$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1A-C2A, 1.472(14); C2A-C3A, 1.366(12); C3A-C4A, 1.489(14); C4A-C5, 1.485(13); C5-C6A, 1.384(15).

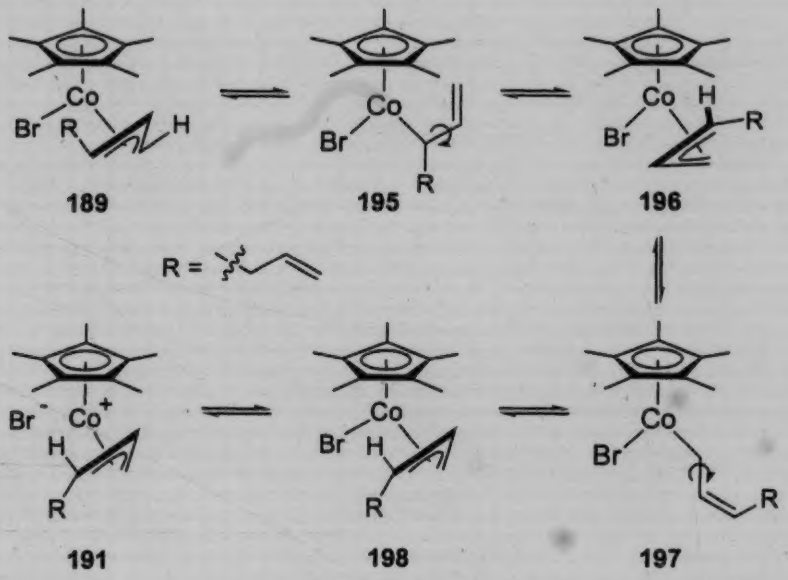
The dihedral angle between the planes defined by C10-C14 and C1A-C3A = 17.4(4)°.

Although the organic halide comprised a mixture of three compounds, none of the *direct* precursors to conjugated byproduct **190** were apparent in the matrix; the formation of complex **190** must therefore result from a rearrangement during or after the formation of nonconjugated allyl complex **189**. One possibility for this rearrangement (Scheme **2.20**) involves the opening of a vacant coordination site on the metal and subsequent coordination of the pendant olefin group to form the cationic intermediate **192**. In order for **192** to form, the allyl moiety in **189** must isomerize to the presumably less-favourable *anti* configuration; this could occur before or after halide dissociation, although it is more likely that this would occur beforehand (Scheme **2.21**), as *syn*/*anti* isomerization normally proceeds via η^1-intermediates that should be less accessible from an electron-deficient cationic 16-electron precursor.

Scheme 2.20



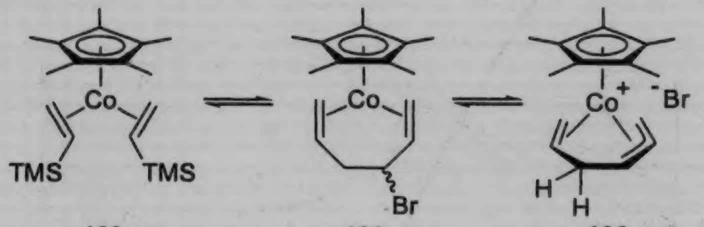
Scheme 2.21



Although the *syn/exo* configuration is thermodynamically preferred for Cp*Co(III) allyl complexes, it is also possible that the *anti/exo* configuration (as in **192**) is kinetically accessed from the oxidative addition process, depending on the mechanism of this oxidation. One plausible mechanism for the oxidative addition involves the formation of the Cp*Co(I) chelated diene complex **199**, which is immediately poised for oxidation to form **196**.

Upon coordination of the olefin functionality, β-hydride elimination and reinsertion can occur to move the olefin into conjugation with the allyl ligand (Scheme **2.20**). Interestingly, after halide association and isomerization to the most stable *syn,exo* configuration, the pendant olefin in complex **190** exhibits the *cis* stereochemistry

Scheme 2.22

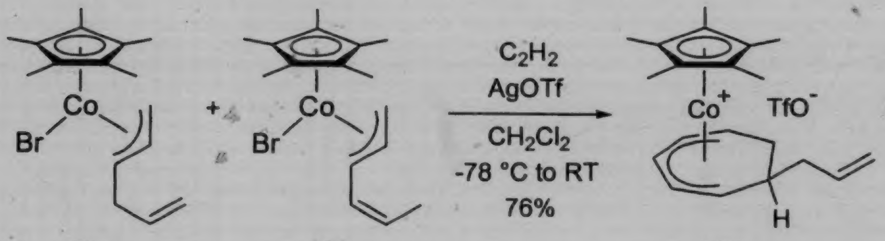


160 **199** **192**

exclusively; the corresponding *trans* stereochemistry would only be accessible via further rearrangement. Gratifyingly, only the *cis* isomer **190** is evident as the contaminant in preparations of the desired allyl complex **189**.

Regardless of the pathway for the formation of **190**, no reaction conditions were found which returned **189** to the exclusion of **190**. In fact, the amount of **190** varied between 5% - 15% of the total Co(III) product between runs that were apparently done under the same conditions; this was also the case when the reaction was attempted with the careful exclusion of ambient light. Although the reaction proceeds efficiently in benzene or toluene, the use of diethyl ether conferred one additional advantage: the very small amount of blue/green paramagnetic material formed during the oxidative addition was far less soluble in ether than in either of the aromatic hydrocarbon solvents. As such, this impurity is readily removed by filtration through Celite when the reaction is performed in ether.

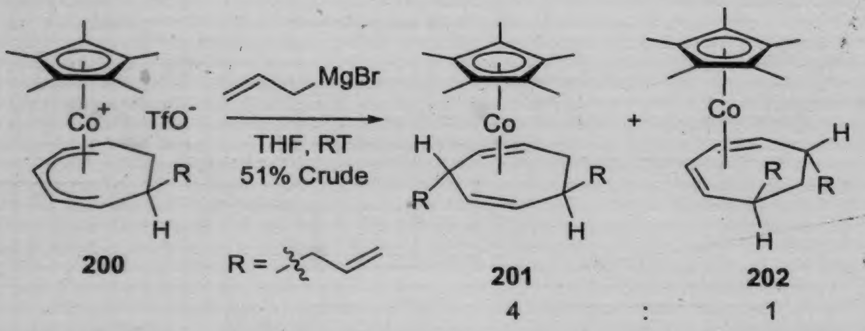
Despite the presence of conjugated isomer **190**, the [3+2+2] cycloaddition of **189** with acetylene was very clean, furnishing the Cp*Co(III) allylcycloheptadienyl complex **200** in high yield and purity (Equation **2.34**), although repeated attempts to recover single crystals of **200** suitable for X-ray crystallography were fruitless. The cycloadduct **200** was isolated to the exclusion of any by-product arising from the presence of **190** in the starting material; this was gratifying, as separation of **190** from **189** could not be achieved.



189 **190** **200**

(Eq 2.34)

With the requisite allylcycloheptadienyl complex **200** in hand, the introduction of the second olefin functionality was then investigated. Unfortunately, all efforts to install the parent allyl functionality at the opposite terminal position met only with frustration. Upon addition of allylmagnesium bromide to **200** at low temperature, a modest amount of pentane-soluble Cp*Co(I) material was recovered. NMR analysis of the crude product matrix revealed, however, that central carbon addition had occurred preferentially to terminal carbon addition (Equation **2.35**), leading to the formation of 3,6-bis(allyl)cyclohepta-1,4-diene complex **201** as the major product.

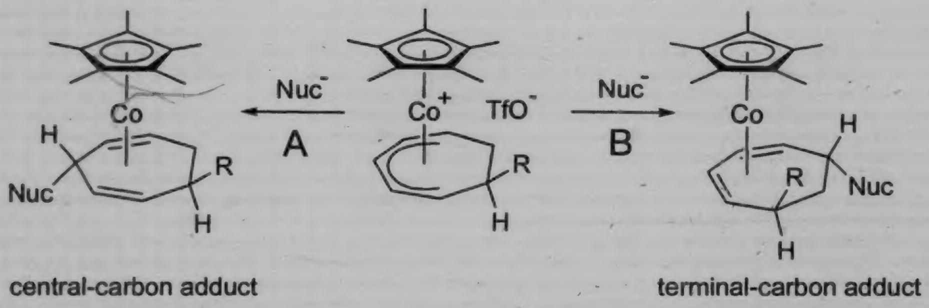

MgBr
Co+
TfO-
THF, RT
51% Crude
R
H
200
R =
Co
H
R
R
H
201
4
:
+
Co
H
R
R
H
202
1

(Eq 2.35)

Other conventional nucleophilic allyl sources proved even less satisfactory, rendering either unreacted starting material (from diallylzinc or tetraallyltin) and/or an intractable paramagnetic product (from allyllithium) which formed, presumably, from a competitive single-electron transfer pathway.

Although some effort had been expended previously by Dzwiniel to investigate the regioselectivity of nucleophilic addition to Cp*Co(III) cycloheptadienyl cations, very little remains known about the factors that govern this selectivity. Addition of hard nucleophiles such as hydride ion principally resulted in central carbon adduct (pathway **A**, Scheme **2.23**) whereas other nucleophiles furnished terminal carbon adduct (pathway **B**).

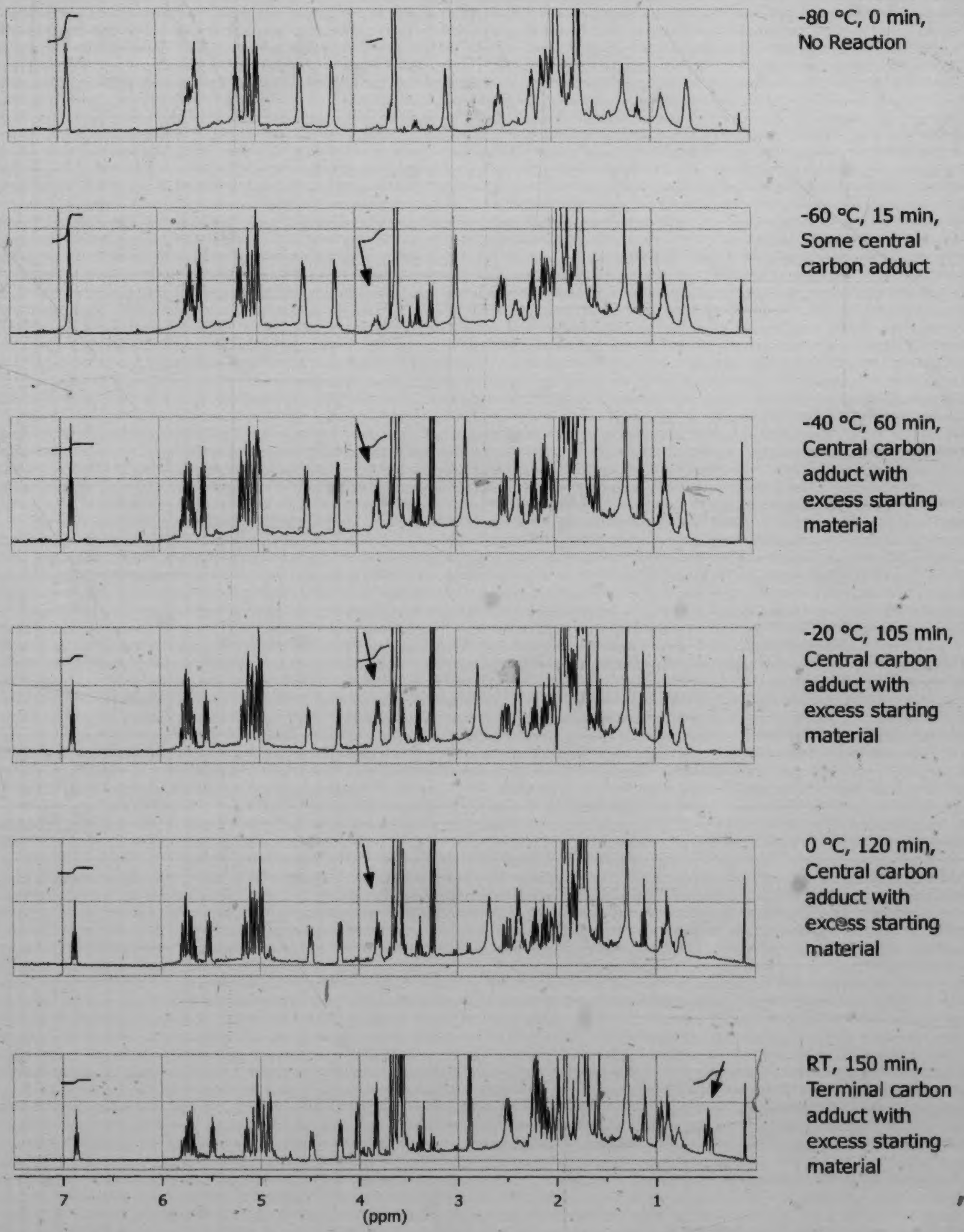
Scheme 2.23


Co
H
Nuc
R
H
central-carbon adduct
Nuc-
A
Co+
TfO-
R
H
Nuc-
B
Co
H
R
Nuc
H
terminal-carbon adduct

One possibility for this disparate regioselectivity is that harder nucleophiles exhibit a kinetic preference for the central cycloheptadienyl carbon whereas softer nucleophiles select kinetically for the terminus of the coordinated moiety; implicit in this proposal is the idea that the central carbon of the ligand is "harder" in nature than the terminus.

Since, however, all of the nucleophiles that yielded terminal carbon adduct were stabilized carbanions such as malonates and enolates, a simpler alternative explanation is that the addition of these nucleophiles is reversible. Therefore, even if stabilized carbanions kinetically select the central carbon of the bound cycloheptadienyl fragment (as per pathway **A**), there may exist a thermodynamic preference for the terminally substituted Co(I) adduct. The terminal Co(I) adduct certainly benefits thermodynamically from additional stabilization as a result of increased backbonding from the d^8 Cp*Co(I) fragment into the conjugated diene moiety. The conjugated diene is itself also more stable than the nonconjugated analogue.

To probe the kinetic regioselectivity of the addition of soft nucleophiles to the Cp*Co(III) cycloheptadienyl template, a low-temperature NMR study was undertaken (Scheme **2.24**). At -80 °C, the addition of malonate anion to **200** in THF-d_8 resulted in no immediate reaction but, on gradual warming to -20 °C over almost 2h, central carbon adduct **203** emerged as the sole observable Co(I) species; excess Co(III) cycloheptadienyl complex **200** was employed, so signals corresponding to this starting material persisted throughout the experiment. The emergence of complex **203** was most conveniently traced by monitoring the multiplet at 3.8 ppm (Figure **2.4**) corresponding to the proton on the 7-



-80 °C, 0 min, No Reaction

-60 °C, 15 min, Some central carbon adduct

-40 °C, 60 min, Central carbon adduct with excess starting material

-20 °C, 105 min, Central carbon adduct with excess starting material

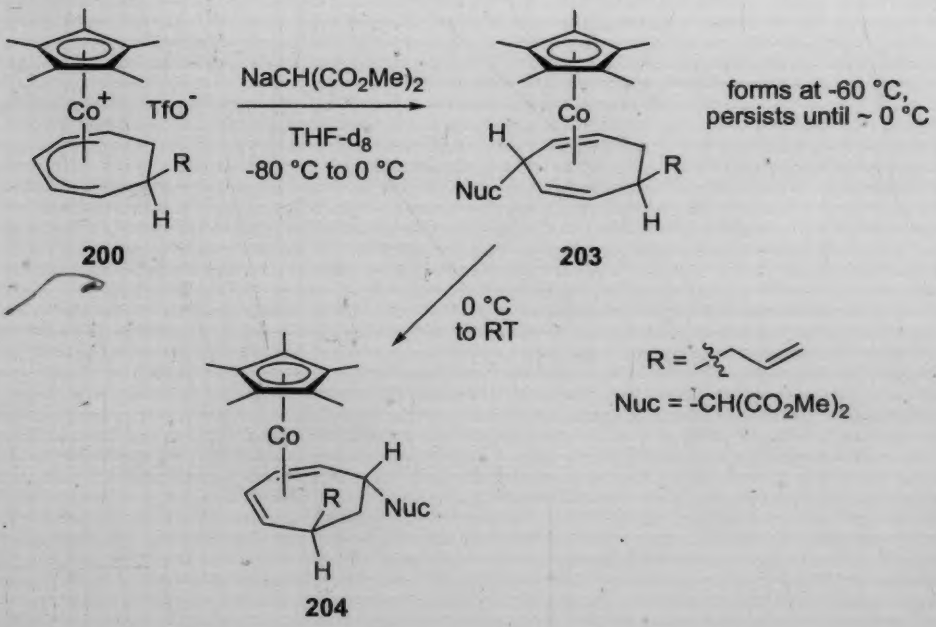
0 °C, 120 min, Central carbon adduct with excess starting material

RT, 150 min, Terminal carbon adduct with excess starting material

Figure 2.1: Variable Temperature ^{1}H NMR Spectra from Addition of Malonate Ion to 200

membered ring at the point of malonate attachment. As the solution was warmed through 0 °C, a methylene proton signal at 0.45 ppm heralded the formation of terminal adduct **204** and, by the time the sample reached room temperature, the replacement of **203** with **204** was complete. The structure of **204** was ultimately verified by X-ray crystallography.

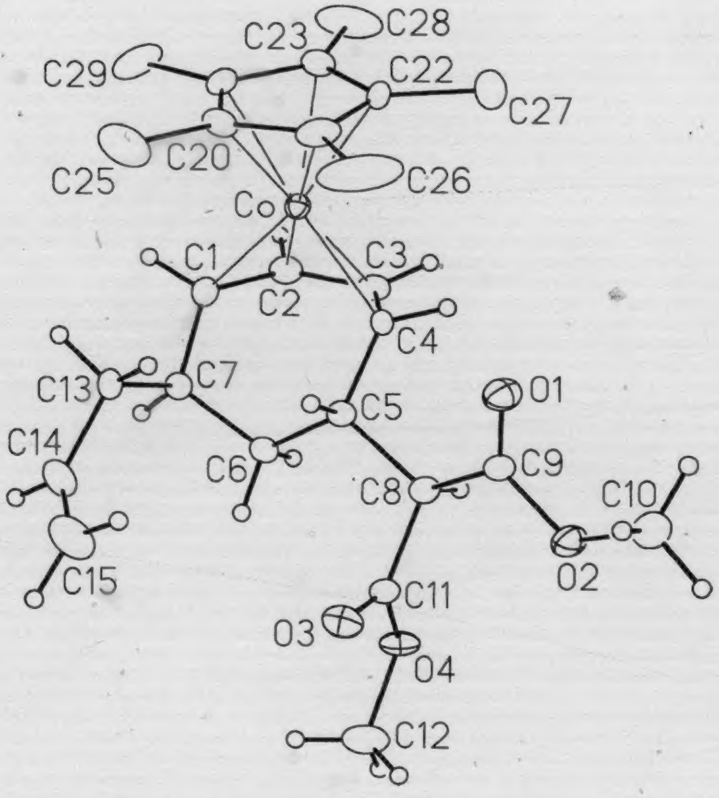
Scheme 2.20



Co+
TfO-
R
H
200
NaCH(CO2Me)2
THF-d8
-80 °C to 0 °C
Co
H
Nuc
R
H
203
forms at -60 °C, persists until ~ 0 °C
0 °C to RT
Co
H
R
Nuc
H
204
R =
Nuc = -CH(CO2Me)2

It is evident from this NMR experiment that central carbon addition is the kinetic preference even for soft nucleophiles and that the terminal carbon adduct only forms from stabilized nucleophiles which add reversibly, ultimately selecting for the more stable conjugated Cp*Co(I) terminal carbon adduct. It is therefore evident that any allyl functionality appended nucleophilically to the terminal electrophilic site of **200** must be introduced as part of a more stabilized nucleophile.

Figure 2.5: ORTEP for Complex **204** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0406


C28
C23
C22
C29
C27
C20
C25
C26
Co
C1
C3
C2
C4
C7
C13
C5
O1
C14
C6
C9
C8
C10
O2
C15
C11
O3
O4
C12

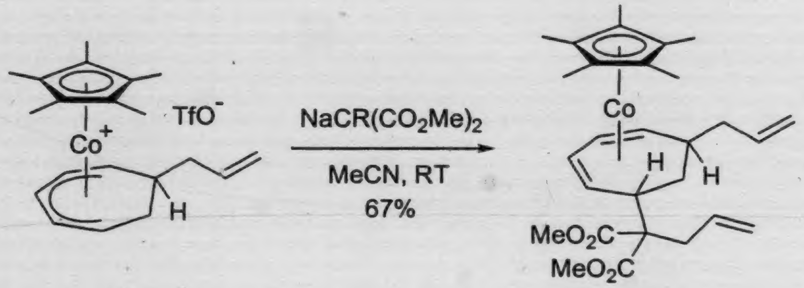
Final Residuals: $R_1 = 0.0723$; $wR_2 = 0.1951$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C2, 1.420(8); C2-C3, 1.407(8); C3-C4, 1.438(8); C5-C8, 1.556(7).

The dihedral angle between the planes defined by C20-C24 and C1-C4 = 8.4(4)°.

In a broader sense, this NMR experiment has illuminated the electrophilic chemistry of Cp*Co(III) cycloheptadienyl complexes in general, resulting in a greater understanding of the factors governing the initial probative nucleophilic additions reported by Etkin and Dzwiniel. In general, if a terminal-carbon adduct is desired, the nucleophile must be capable of adding reversibly under the reaction conditions; stabilized carbanions are thus the most obvious candidates.

With this in mind, the cationic Cp*Co(III) cycloheptadienyl complex **200** was treated with a solution of the sodium salt of allyl dimethyl malonate (Equation **2.36**). The terminal adduct **205** was isolated from the reaction after crystallization from pentane. Although complex **205** is significantly more soluble in pentane than other Cp*Co(I) diene complexes such as **172** and **173**, a moderate yield of deep red crystalline **205** was recovered in a form suitable for X-ray crystallography (Figure **2.6**).

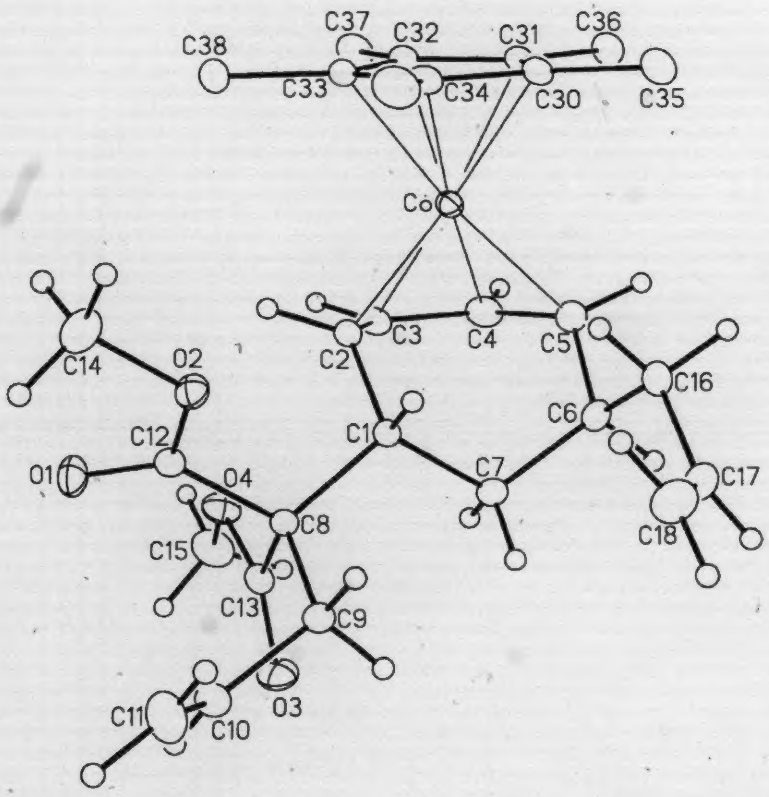


200 **205**

(Eq 2.36)

Efforts to cyclize **205** using conventional conditions for olefin metathesis failed entirely, furnishing only unreacted Co(I) starting material, although small amounts of decomposition were evident in all cases. This same unsatisfying result was realized when the more reactive Grubbs-Hoveyda catalyst[138,139] **206** was alternatively employed, and the

Figure 2.6: ORTEP for Complex **205** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0325


C37
C32
C31
C36
C38
C33
C34
C30
C35
Co
C14
O2
C3
C4
C5
C2
C16
C6
C12
C1
O1
O4
C7
C17
C8
C15
C18
C13
C9
O3
C11
C10

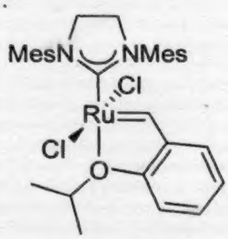
Final Residuals: $R_1 = 0.0339$; $wR_2 = 0.0944$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C8, 1.578(2); C2-C3, 1.434(3); C3-C4, 1.419(3); C4-C5, 1.422(3).

The dihedral angle between the planes defined by C30-C34 and C2-C5 = 6.05(15)°.

The dihedral angle between the planes defined by C2-C5 and C1, C2, C5 & C6 = 45.67(8)°.

The dihedral angle between the planes defined by C1, C2, C5 & C6 and C1, C6, & C7 = 53.53(18)°.



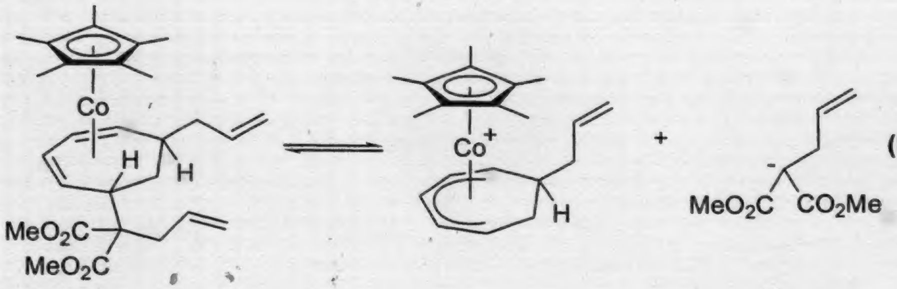
206: Grubbs'-Hoveyda Catalyst

lack of olefin metathesis could not be remedied by modifying the reaction temperature, solvent, or concentration.

One possibility for the failure to recover metathesis products from **205** is the potential for electron transfer to occur from the Co(I) center to the ruthenium catalyst, thereby deactivating the catalyst. With this in mind, attempts were made to oxidatively decomplex the cycloheptadiene ligand from **205** with an eye to effecting a ring-closing metathesis on the non-templated organic compound. Surprisingly, photolysis of **205** in the presence of allyl bromide also returned slightly decomposed starting material as the only identifiable product.

One other curious observation was made regarding complex **205**, which potentially sheds some light on the inability of this complex to undergo olefin metathesis chemistry or oxidative decomplexation. Whereas most Cp*Co(I) diene complexes are readily purified by passage through a column or plug of deactivated alumina by hydrocarbon solvent, complex **205** failed to elute under these mild conditions.

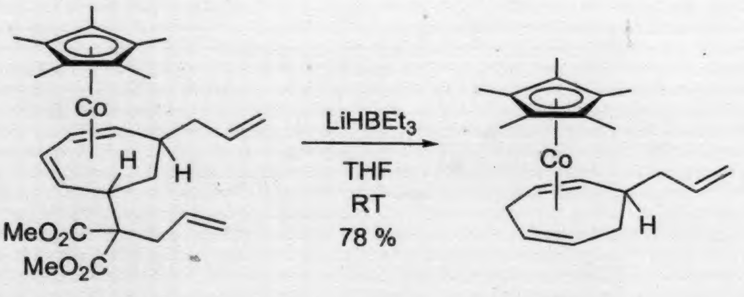
Owing to the considerable steric bulk of the allyl dimethylmalonate nucleophile and the fact that it forms a quaternary center upon addition to **200**, it is quite likely that the dissociation of this fragment occurs readily in solution (Equation **2.37**). As such, under metathesis conditions, a small amount of allyl malonate anion **207** will be present



205 **207** **(Eq 2.37)**

to react with and, presumably, deactivate the metathesis catalyst. As well, under photolytic conditions, the dissociation equilibrium could shift to favor the Co(III) species which would be unable to oxidatively decomplex the seven-membered ring and react with the added allyl bromide. Finally, reversion to the Cp*Co(III) cycloheptadienyl cation would explain the resistance of **205** to elution through an alumina column.

In an effort to reduce the ester functionalities in **205** to alcohols and thereby render the fragment unable to dissociate from the Cp*Co(I) complex, a solution of complex **205** in ether was treated with Super Hydride™ (Equation **2.38**). Interestingly, no diol was isolated from the reaction mixture; instead, the non-conjugated Cp*Co(I) complex **208** was cleanly formed. The formation of **208**, although disappointing, confirms that the bulky allyl dimethylmalonate fragment rapidly dissociates from the Cp*Co(I) cycloheptadiene fragment in solution. Although nucleophilic anion stability has been identified as a requirement for terminal carbon addition to Cp*Co(III) cycloheptadienyl complexes (*vide supra*), it is evident that, if the rate and/or extent of reversion is too great, further elaboration of the carbon skeleton will be impeded.

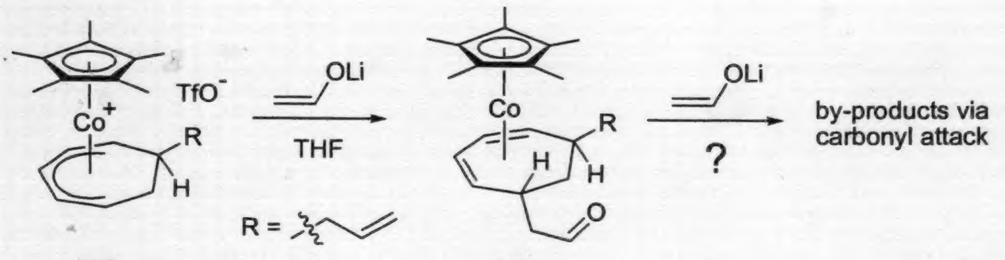


205 **208**

(Eq 2.38)

A number of other approaches were taken in an effort to selectively elaborate the terminus of the cycloheptadienyl fragment with an olefin or olefin-precursor; unfortunately, however, none of these efforts bore fruit. With an eye to preparing the carbonyl-bearing complex **209**, complex **200** was added to a solution of acetaldehyde-enolate[140-143] (Scheme **2.25**). Unfortunately, no tractable Co(I) product was recovered from this reaction. Similarly, addition of the lithium enolate of methyl vinyl ketone was also non-productive. In each case, the failure to generate clean product may perhaps be a result of a competing electron-transfer process, as Dzwiniel also experienced difficulty and/or low yields in the addition of such nucleophiles to Cp*Co(III) templates. Another possible difficulty is the potentially low relative reactivity of the cycloheptadienyl fragment compared to the nascent carbonyl functionality in the desired product. Even if **209** were to form from **200**, for example (Scheme **2.25**), the resulting organometallic aldehyde might itself be susceptible to reaction with enolate at a rate likely far greater than **200**, although this remains to be determined.

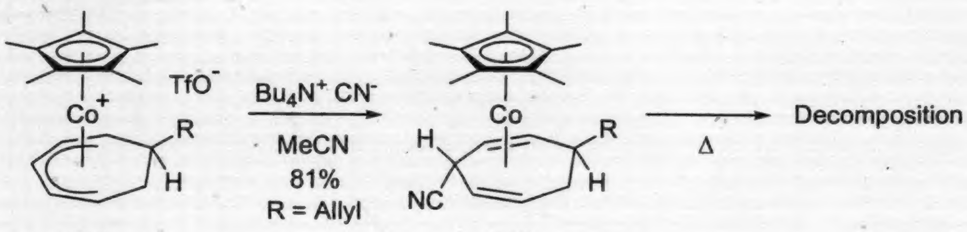
Scheme 2.25


TfO-
Co+
R
H
OLi
THF
R =
Co
R
H
H
O
OLi
?
by-products via carbonyl attack

200 **209**

The hard but weakly basic cyanide nucleophile was also added to **200** but, unfortunately, it too selected for the central carbon (Scheme **2.26**). Attempts to thermally isomerize the non-conjugated product **213** were frustrated by the decomposition of the Co(I) material. Even efforts to catalyze this thermal isomerization by addition of triphenylborane[144,145] and perfluorotriphenylborane were unproductive.

Scheme 2.26


TfO-
Co+
R
H
Bu4N+ CN-
MeCN
81%
R = Allyl
Co
H
NC
R
H
Δ
Decomposition

200 **213**

The failure of **213** to isomerize to terminal carbon adduct, while disappointing, reveals another important aspect of the general nucleophilic addition to Cp*Co(III) cycloheptadienyl complexes. Although stabilized anions such as malonates and enolates ultimately yield terminal adducts, anion stability is not the only factor that determines the reversibility of the kinetically favourable central-carbon addition.

Although cyanide ion is significantly less basic than malonate or enolate, its irreversible addition implies that the hardness and, perhaps, steric profile of the nucleophile are also important in promoting isomerization from coordinated 1,4-diene to 1,3-diene.

Part H: Summary and Outlook

Although the [3+2+2] cycloaddition has been successfully harnessed as a pathway into bicyclic organic molecules with seven-membered rings, the modest yield of the key cycloaddition step – particularly in those cases bearing a methyl group on the central allyl carbon – is disappointing, and current research in the Stryker group is focused on developing alternatives that furnish complexes akin to **161** and **162** in higher yield and in greater purity. That more highly-substituted Cp*Co(III) allyl complexes are often prone to a competitive decomposition is a problem that was also identified by Dzwiniel, and it may be that an entirely new transition metal template will yield the best results. Dzwiniel's work has shown that the nature of the cyclopentadienyl ancillary ligand is crucial in the [3+2+2] cycloaddition, and the ideal balance of steric and electronic effects has yet to be identified.

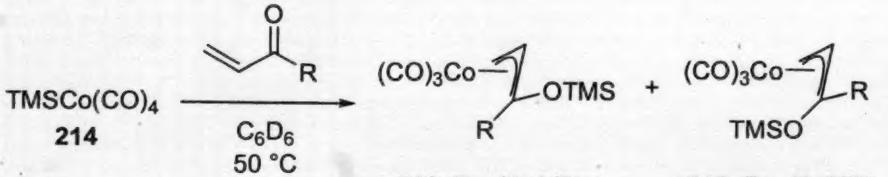
The decomplexation of cycloheptadiene ligands from the Cp*Co(I) template has been successfully accomplished with a photolytic oxidative addition of allyl bromide. Apart from furnishing the organic target molecules is high yield, the method also allows for recovery of the template in an immediately useful form, although only a small number of these decomplexations have, to date, been attempted. More work in this area would hopefully elucidate the mechanism of the decomplexation as well, and perhaps identify conditions tolerant of more highly substituted allyl complexes.

Chapter 3 – Oxygen-Bearing Seven-Membered Carbocycles

Section 1: Introduction

Part A: 1-Hydroxyallyl and 1-Silyloxyallyl Chemistry

Murai[146] was the first to report the synthesis and spectral properties of transition metal complexes bearing a silyloxyallyl ligand in 1983. Treatment of the cobalt tetracarbonyl complex **214** with acrolein or methyl vinyl ketone afforded the substituted Co(III) silyloxyallyl complexes **215 - 218** in moderate yields (Equation **3.1**). In either case, a mixture of *syn-* and *anti-* isomers was obtained, with the product stereochemical configuration assigned on the basis of ^{1}H NMR chemical shifts and coupling constants. In the case of the product derived from acrolein, the allyl proton attached to the oxygen-bearing carbon is diagnostic, appearing as a doublet (J = 7 Hz) at 5.01 ppm in the *syn*-isomer **215** and as a more deshielded and narrower doublet (J = 3.5 Hz) at 6.17 ppm in the *anti*-isomer **216**. This diagnostic proton is absent in the methyl vinyl ketone adduct and, as such, the product stereochemical assignment in this case must be considered



(Eq. 3.1)

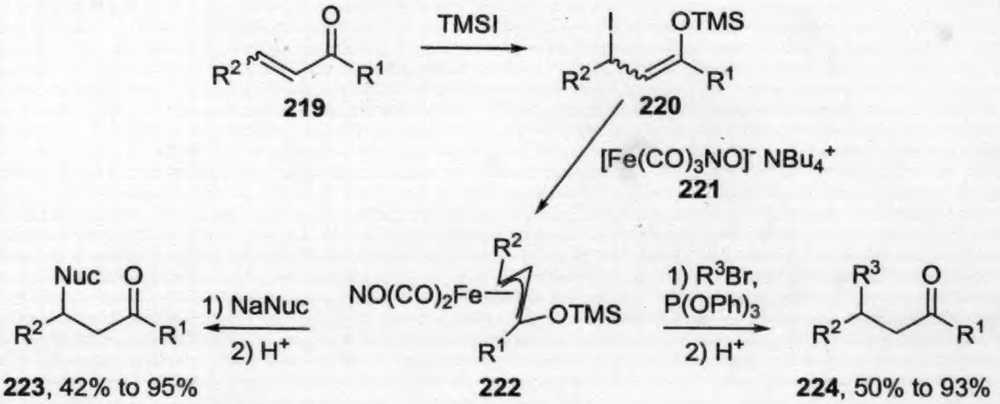
215: R = H, 44%
217: R = Me, 12%

216: R = H, 20%
218: R = Me, 46%

tenuous at best. Murai did not explore the chemistry of these allyl complexes beyond their preparation and ^{1}H NMR characterization in an NMR tube; yields were estimated by integration against an internal standard.

Otsuji[147-149] has reported the interesting chemistry of iron silyloxyallyl complexes prepared from α,β-unsaturated ketones. The organometallic Fe(II) silyloxyallyl complexes **222** are generated from an oxidative addition of the TMS-protected allyl iodides **220** to the highly reduced ferrate complex **221** (Scheme **3.1**). The Fe(II) allyl complexes **222** were not isolated and no spectroscopic details were reported, except for several infrared absorptions. Nonetheless, Otsuji demonstrated that the putative Fe(II) silyloxyallyl complexes **222** were competent synthetic equivalents of β-acyl carbocations, in that stabilized carbon nucleophiles such as dialkylmalonates added selectively to the allyl terminus distal to the oxygen atom to afford, upon acidic hydrolysis, Michael-type adducts **223**.

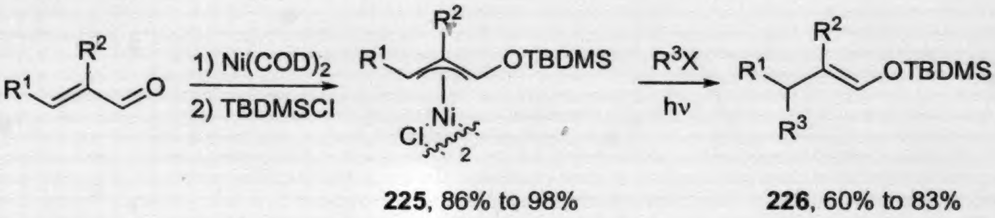
Scheme 3.1



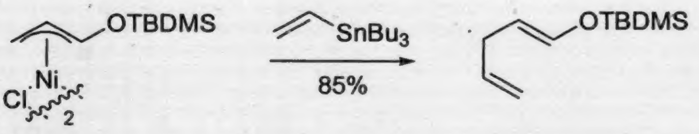
Interestingly, the same Fe(II) silyloxyallyl complexes **222** functioned as β-acyl *carbanion* equivalents as well, reacting with electrophilic propargyl and allyl bromides to furnish β-substituted ketones **224** in moderate yields. Again, reactivity at the silyloxyallyl ligand was selective for carbon-carbon bond formation at the terminus furthest from the silyloxy group.

Drawing on the previously established utility of allylnickel reagents for coupling with halocarbon electrophiles,[150-154] Mackenzie has reported[155,156] the use of silyloxyallyl nickel complexes for carbon-carbon bond formation. Reaction of α,β-unsaturated aldehydes with $Ni(COD)_2$ followed by addition of TBDMSCl afforded Ni(II) silyloxyallyl complexes **225** as burgundy-red crystalline solids, which have been well characterized and studied by X-ray crystallography (Scheme **3.2**). These Ni(II) silyloxyallyl compounds are dimeric and react with aryl bromides, alkenyl bromides, isobutyryl chloride, as well as primary and secondary iodides to afford decomplexed silyl enol ethers **226** which bear substitutents at the β-position. In most cases, the *E*:*Z* ratio of the chromatographed product **226** was better than 20:1, and the alkylations were completely regioselective for the allyl terminus furthest from the oxygen.

Scheme 3.2



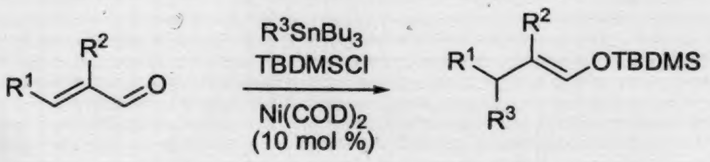
Mackenzie also reported the amphiphilic nature of the Ni(II) silyloxyallyl complexes by coupling them with weakly *nucleophilic* vinyl- and acyl-tin reagents (Equation **3.2**). Since Ni(0) was consumed in the formation of the Ni(II) silyloxyallyl reagent but then liberated upon reaction with the tin reagent, Mackenzie was able to employ a catalytic amount of Ni(0) to successfully mediate the overall process (Equation **3.3**).



225a **226a**

(Eq. 3.2)

Mackenzie suggests that the carbon-carbon bond is formed through a transmetallation of the vinyl- or acyl-tin reagent with the Ni(II) silyloxyallyl complex to generate an intermediate vinyl- or acyl Ni(II) silyloxyallyl species; a subsequent reductive elimination expels the product and regenerates the Ni(0).



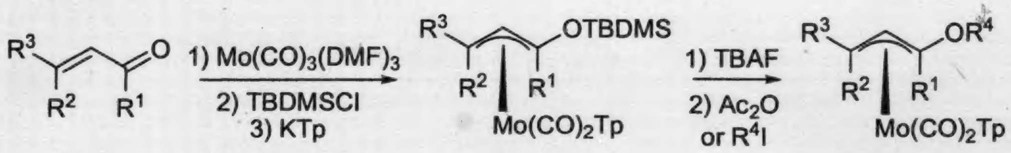
226, 48% to 79%

(Eq. 3.3)

Liebeskind[157] has prepared trispyrazolylborate carbonyl complexes **227** of molybdenum featuring silyloxyallyl ligands in a stepwise one-pot procedure from

$Mo(CO)_3(DMF)_3$. Liebeskind's study was primarily concerned with the spectroscopy of these complexes, as well as the interconversion of the various allyl configurations; very little of the chemistry of the molybdenum silyloxyallyl compounds was described. Of note, however, is the desilylative conversion of the silyloxy group to ester or ether functionalities (e.g. **228**), in modest to good yield.

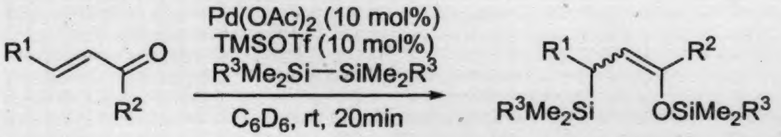
Scheme 3.3


R3
O
R2
R1
1) Mo(CO)3(DMF)3
2) TBDMSCl
3) KTp
R3
OTBDMS
R2
R1
Mo(CO)2Tp
1) TBAF
2) Ac2O
or R4I
R3
OR4
R2
R1
Mo(CO)2Tp

227 37% - 87%

228 19% - 88%
R_4 = Ac, Me, or *i*-Pr

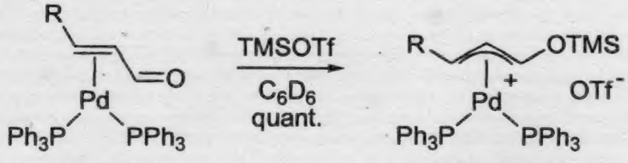
Kurosawa[158] has recently described the bis-silylation of α,β-unsaturated carbonyl compounds via a Pd(0)-catalyzed sequence (Equation **3.4**). Silyl enol ethers **229** - **232** were formed as mixtures of stereoisomers; E/Z ratios were reported for each product and vary widely from substrate to substrate.


R1
O
R2
Pd(OAc)2 (10 mol%)
TMSOTf (10 mol%)
R3Me2Si—SiMe2R3
C6D6, rt, 20min
R1
R2
R3Me2Si
OSiMe2R3

(Eq. 3.4)

229: $R^1 = R^2 = H$, $R^3 = Ph$, 99%, E/Z = 58/42
230: $R^1 = H$, $R^2 = Me$, $R^3 = Ph$, 99%, E/Z = 69/31
231: $R^1 = Ph$, $R^2 = Me$, $R^3 = Ph$, 40%, E/Z = 30/70
232: $R^1 = Ph$, $R^2 = Me$, $R^3 = Me$, 99%, E/Z = 18/82

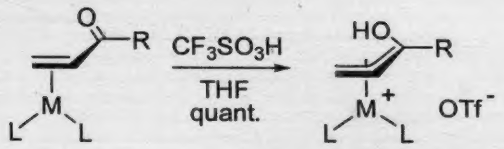
Kurosawa proposes the intermediacy of a silyloxyallyl palladium complex in the formation of these products, although no such intermediate has ever been directly observed or isolated. Evidence for this sort of species has been provided, however, by the quantitative formation of the more stable bis-phosphine analogues **233** and **234** (Equation **3.5**) under reaction conditions similar to those employed in the bis-silylation reactions.



233: R = H
234: R = Ph

(Eq. 3.5)

Although the chemistry of transition metal allyl complexes has been well investigated, very little work at all has been focused on the chemistry of 1-hydroxyallyl complexes. Indeed, the only literature report of well-characterized 1-hydroxyallyl complexes appeared in 2002. Kurosawa and coworkers[159] prepared a small number of 1-hydroxyallyl complexes of palladium and platinum **235 - 240** by quantitative protonation of the corresponding low valent α,β-unsaturated carbonyl complexes (Equation **3.6**). Apart from this report, the only other example of a η^3-1-hydroxyallyl complex is a nickel species described by Jolly and Wilke[160] in their survey of the organic chemistry of nickel; the original investigators did not publish the synthesis or characterization of this compound.[161]


O
R
M
L
L
CF3SO3H
THF
quant.
HO
R
M
+
L
L
OTf-

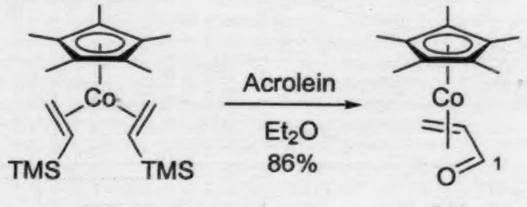
(Eq. 3.6)

235: M = Pd, R = Me, L_2 = DPPF
236: M = Pd, R = H, L = PPh_3
237: M = Pd, R = Me, L = PPh_3
238: M = Pt, R = Me, L_2 = DPPF
239: M = Pt, R = H, L = PPh_3
240: M = Pt, R = Me, L = PPh_3

Section 2: Results and Discussion

*Part B: Synthesis and Characterization of Cp*Co(III) Hydroxyallyl Complexes*

The success of Kurosawa and co-workers in the synthesis of 1-hydroxyallyl complexes prompted an investigation of an analogous pathway in the Cp*Co system. The novel Cp*Co(I) acrolein complex **241** was readily synthesized in high yield by ligand exchange from the labile Cp*Co(I) source **160**.[126-128] It is noteworthy that excess acrolein was tolerated with no evidence for the competitive formation of a bis(η^2-acrolein) complex. The deep green acrolein complex **241** was purified by crystallization from pentane and was very air sensitive, both as a solid and in solution. Repeated attempts to grow crystals suitable for X-ray diffraction were met with frustration. Additionally, the air-sensitivity of **241** was such that repeated efforts to obtain elemental analysis results within publishable limits failed, although ^{1}H NMR spectroscopy indicated that this complex was obtained in high purity; **241** was used in subsequent experiments without purification beyond the crystallization described above.

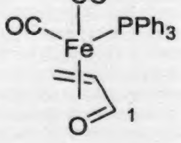


(Eq. 3.7)

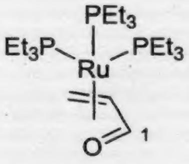
In principle, the η^4-acrolein complex **241** could adopt either an s-*cis* or s-*trans* configuration. In the case of η^4-butadiene complexes of transition metals, it is known that the vast majority of such complexes thermodynamically adopt the s-*cis* configuration, with few exceptions. The only known examples of first-row transition metal butadiene complexes in the s-*trans* configuration have recently been prepared in the Stryker group;[162,163] all other s-*trans* complexes are restricted to the second and third rows of the transition series.

By extension, it seems most likely that complex **241** adopts the s-*cis* configuration. In the absence of crystallographic data, the best indication of this stereochemistry should arise from the magnitude of the vicinal coupling interaction between H_1 and H_2. In complex **241**, however, this value is approximately 0.6 Hz and, as such, provides no definitive indication of the geometry. Such a low value is mainly due to the electron withdrawing nature of the oxygen atom, but must also reflect the dihedral angle between the vicinal protons H_1 and H_2.

Some support for the s-*cis* configuration in **241** is provided by the corresponding coupling constants obtained from the literature compounds **242** and **243**. These compounds are the only reported α,β-unsaturated aldehyde complexes for which both X-ray structural data and ^{1}H NMR data are available. In the case of iron(0) complex **242**, the aldehyde proton (H_1) exhibits a coupling magnitude of 1.2 Hz,[164] whereas in ruthenium(0) complex **243**,[165] the corresponding coupling interaction is so weak that the proton is described only as a broad singlet.

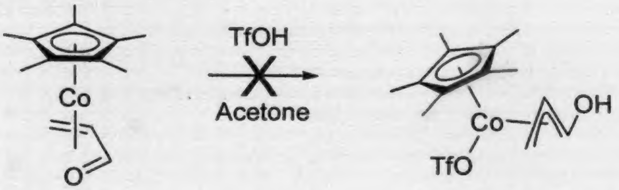


242



243

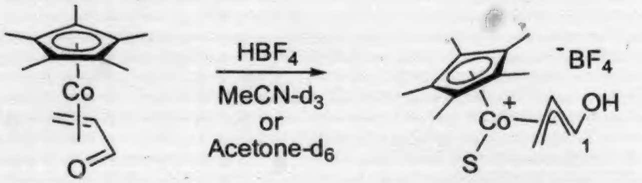
One attempt was made to prepare the 1-hydroxyallyl inner-sphere triflate complex **244** by triflic acid protonation of **241** in acetone (Equation **3.8**). Although the solution changed rapidly in colour from green to purple-brown, suggestive of allyl formation, attempts to isolate and characterize **244**, or any other isolable organocobalt species, failed. Simple Cp*Co(III) allyl triflate complexes have been previously prepared by Etkin and Dzwiniel (*vide supra*, Chapter 2 of this thesis), and found to be somewhat unstable.[17,94,95] It is quite possible that the corresponding 1-hydroxyallyl complex requires a coordinating solvent to occupy the vacant co-ordination site that exists in **244** when such a weakly coordinating ligand such as triflate is present.



241 **244**

(Eq. 3.8)

To test this premise, solutions of **241** in deuterated acetonitrile and deuterated acetone were each treated with a single equivalent of $HBF_4{\cdot}OEt_2$ (Equation **3.9**). The use of the deuterated coordinating solvent permitted NMR interrogation of the protonation



241

245: S = MeCN-d$_3$
246: S = Acetone-d$_6$

(Eq. 3.9)

products **245** and **246** without removal of the polar coordinating solvent, which may well be essential for the stability of the cationic Cp*Co(III) hydroxyallyl complex.

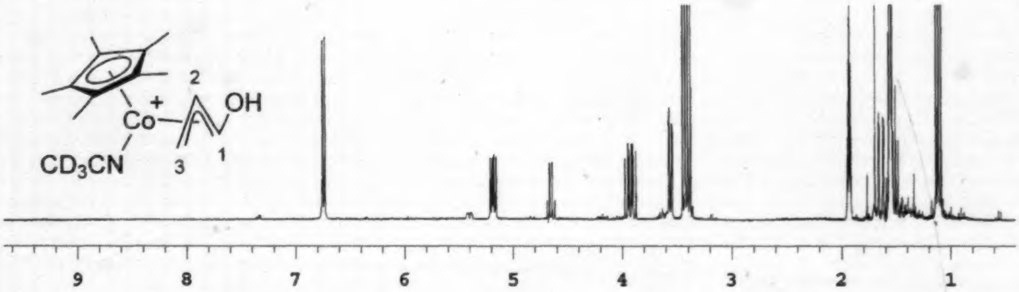
Protonation in acetonitrile-d$_3$ afforded a single major product, which appears to be the desired cationic complex **245**, likely stabilized with an inner-sphere solvent molecule. The ^{1}H NMR data for the major product are listed in Table **3.1**. There also appears to be an approximately 10% excess of HBF$_4$ etherate present, as well as a small amount of an unidentified by-product, as illustrated in Figure **3.1**.

Table 3.1: ^{1}H NMR Data for Compound **245**

	H_1	H_2	H_{3syn}	H_{3anti}	H_{OH}	H_{Cp*}
δ (ppm)	5.18 (dd)	3.92 (ddd)	3.56 (ddd)	1.64 (dm)	6.74 (d)	1.55
J (Hz)	9.7, 6.2	12.3, 9.7, 8.1	8.1, 1.5, 0.6	12.3	6.2	-

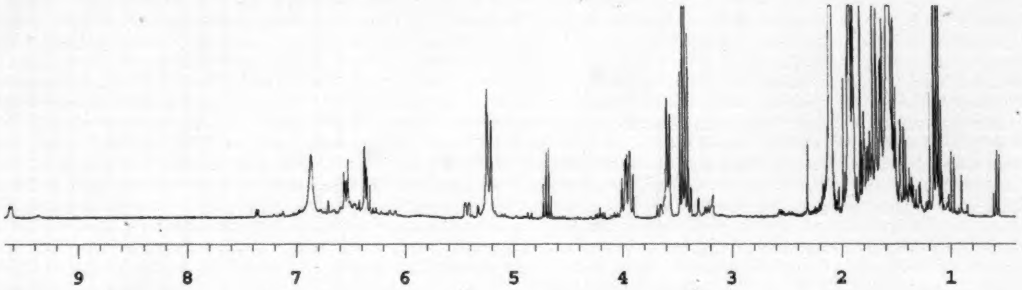
Interestingly, a 6.2 Hz coupling was observed between the hydroxy proton appearing at 6.74 ppm and the adjacent allyl proton at 5.18 ppm. The stereochemistry of this allyl complex is tentatively assigned as *syn*, owing to the 9.7 Hz coupling between H$_1$ and the with the central allyl proton (H$_2$). The *anti* and *syn* protons at the other terminus of the allyl fragment respectively exhibit couplings of 12.3 Hz and 8.1 Hz with the central allyl proton. The electronegative oxygen atom would be expected to *diminish* the magnitude of coupling interactions of the adjacent allyl proton.

Figure 3.1: ^{1}H NMR Spectrum of **245** Formed *In Situ* in Acetonitrile-d_3 (solvent: δ 1.95)



To probe the reactivity of the hydroxyallyl complex **245** with an alkyne, the solution generated in an NMR tube was treated with a stream of acetylene gas and allowed to rest at room temperature for one hour. For the most part, the hydroxyallyl complex **245** remained unchanged, although a number of unassigned new peaks began to grow in (Figure **3.2**). None of the new resonances, however, suggested the formation of a seven-membered ring product. Notably, the H/D exchange of the acidic OH proton was observed.

Figure 3.2: ^{1}H NMR Spectrum of **245** After Acetylene Stream



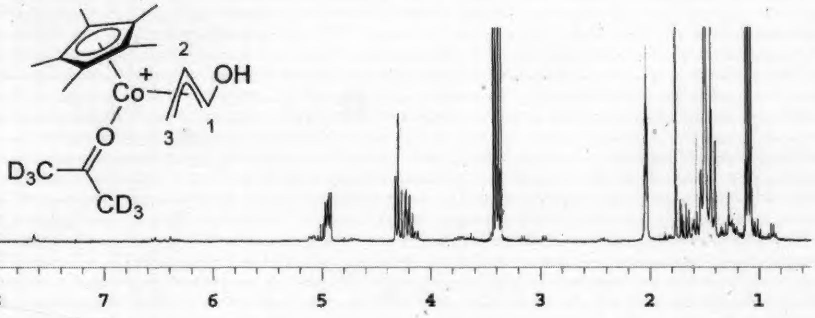
Protonation of **241** in deuterated acetone also yielded the solvated cationic hydroxyallyl complex **246** as the major product (Equation **3.9**), although the ^{1}H NMR spectrum, summarized in Table **3.2**, revealed that this reaction was not as clean as the acetonitrile run (Figure **3.3**).

Table 3.2: ^{1}H NMR Data for Compound **246**

	H_1	H_2	H_{3syn}	H_{3anti}	H_{OH}	H_{Cp^*}
δ (ppm)	4.94 (dd)	4.22 (ddd)	4.31 (d)	1.43 (d)	8.62 (d)	1.50
J (Hz)	9.3, 6.0	11.7, 9.3, 8.2	8.2	11.7	6.0	-

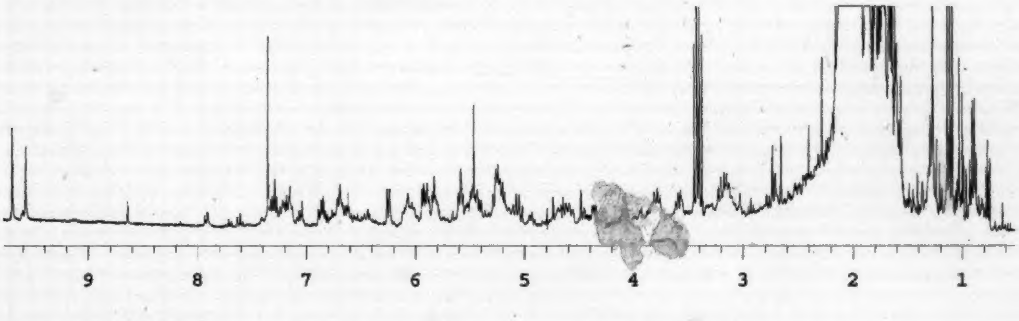
The stereochemistry of the hydroxy group is again assigned as *syn*, based on a value of 9.3 Hz for the coupling of the adjacent allyl proton (H_1) with H_2. Treatment of this reaction mixture with acetylene resulted in the rapid consumption of the hydroxyallyl complex, but unfortunately the formation of an intractable mixture of unidentified products (Figure **3.4**).

Figure 3.3: ^{1}H NMR Spectrum of **246** Formed *In Situ* in Acetone-d$_6$ (solvent: δ 2.04)

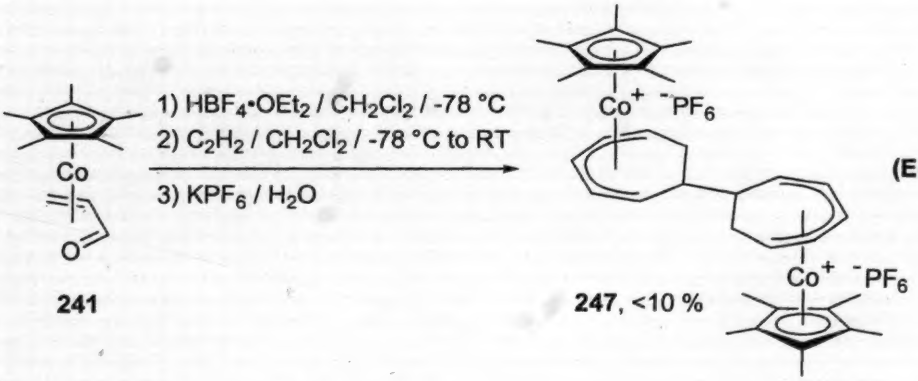


It is noteworthy that the acetone-solvated cationic Co(III) hydroxyallyl complex was much more reactive towards acetylene; presumably acetonitrile is a superior ligand to acetone for the cationic complex, and the acetone dissociates much more readily to vacate a coordination site for the incoming acetylene molecule.

Figure 3.4: ^{1}H NMR Spectrum of **246** After Acetylene Stream



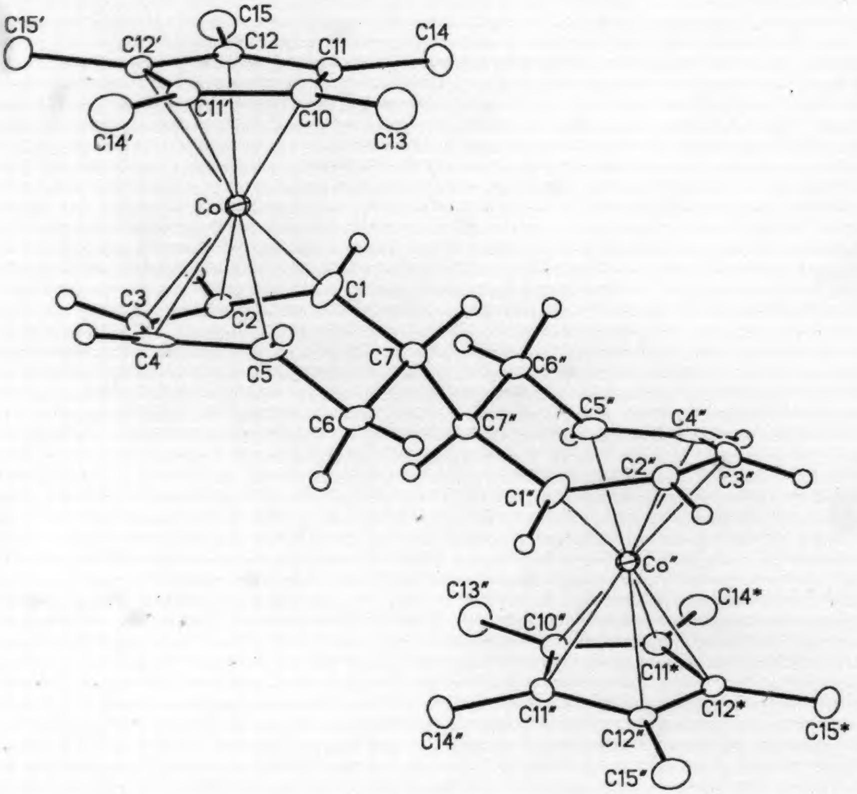
Dichloromethane was also assayed as a non-coordinating solvent for the formation and cycloaddition reaction of the 1-hydroxyallyl Cp*Co(III) cation. Acrolein complex **241** was protonated with $HBF_4{\cdot}OEt_2$ at -78 °C and then treated with an excess of acetylene, before being allowed to warm to room temperature overnight. Interestingly, the only identifiable product obtained from the reaction was dimeric dicationic complex **247**, which was isolated as orange-red crystals suitable for X-ray crystallography after anion exchange with hexafluorophosphate (Equation **3.10**). Only a few milligrams were recovered, and the yield was less than 10%; an accurate yield for this compound was not obtained. No oxygen-containing product was recovered from the reaction.


Co
1) HBF4•OEt2 / CH2Cl2 / -78 °C
2) C2H2 / CH2Cl2 / -78 °C to RT
3) KPF6 / H2O
Co+ -PF6
Co+ -PF6
241
247, <10 %

(Eq. 3.10)

The mechanism for the formation of the dimer **247**, even in low yield, is puzzling. Clearly, any such mechanism will most likely involve [3+2+2] cycloaddition to furnish the seven-membered rings observed in complex **247**. Additionally, loss of an oxygen atom from each half of the dimer must also be accounted for, as well as the eventual coupling of the two organocobalt fragments.

Figure 3.5: ORTEP for Complex **247** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0304


C15'
C15
C12'
C12
C11
C14
C11'
C10
C14'
C13
Co
C1
C3
C2
C4
C5
C7
C6"
C6
C7"
C5"
C4"
C2"
C3"
C1"
Co"
C13"
C14*
C10"
C11*
C11"
C12*
C14"
C12"
C15*
C15"

Final Residuals: $R_1 = 0.0434$; $wR_2 = 0.1089$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Primed atoms are related to unprimed atoms by an inversion center

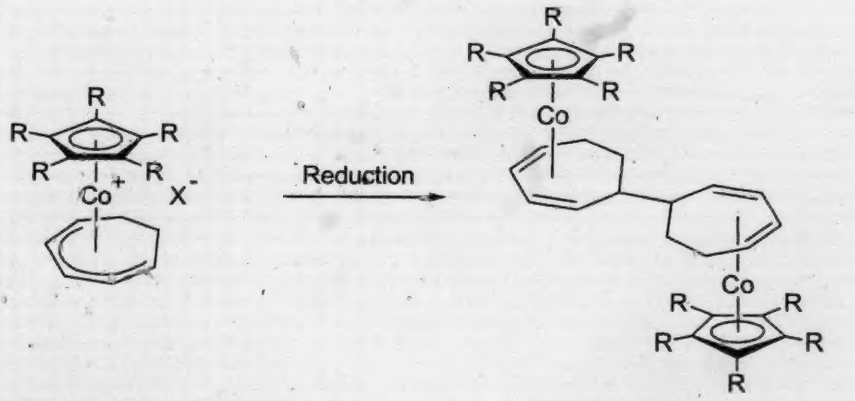
Selected Bond Distances (Å): C7-C7", 1.564(11); C1-C7, 1.49(2); C6-C7, 1.520(8).

Selected Bond Angles (deg.): C1-C7-C7", 112.5(8).

Selected Torsional Angles (deg.): C1-C7-C7"-C1", 180; C6-C7-C7"-C6", 180; C1-C7-C7"-C6", 62.55.

The radical coupling of polyolefinic ligands of 19-electron organometallic complexes is a well-established process and has been the subject of comprehensive reviews.[166,167] Indeed, Salzer[168] has reported the formation of a closely-related Co(I) dimer **250** from the reduction of the parent CpCo(III) cycloheptadienyl cation **248** (Equation **3.11**); the analogous Cp* dimer **251** has since been prepared by Dzwiniel[17] in the Stryker group.

Assuming that the [3+2+2] cycloaddition proceeds as expected to furnish at least some of the desired product **253**, a mechanism for the dimerization of the carbon skeleton can be envisioned that assumes the presence of some unreacted Cp*Co(III) hydroxyallyl cation **252** (Scheme **3.4**). Previous work by Dzwiniel and Etkin suggests that the initial allyl-alkyne migratory coupling is the rate-limiting step in the [3+2+2] cycloaddition and that, as such, it is reasonable to anticipate a mixture of product cycloheptadienyl **253** and unreacted cationic **252** in an incomplete [3+2+2] reaction.

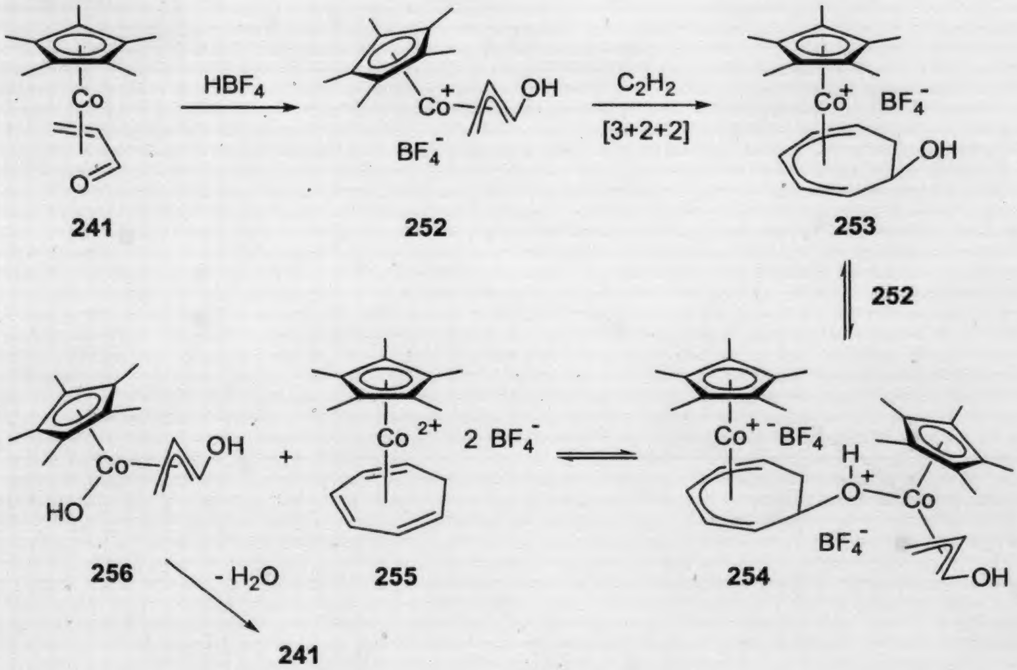


(Eq. 3.11)

248: R = H, X = PF_6
249: R = Me, X = OTf

250: R = H
251: R = Me

Scheme 3.4


Co
O
241
HBF$_4$
Co$^+$
OH
BF$_4^-$
252
C$_2$H$_2$
[3+2+2]
Co$^+$
BF$_4^-$
OH
253
252
Co
OH
HO
256
- H$_2$O
241
+
Co $^{2+}$
2 BF$_4^-$
255
Co$^+$ $^-$BF$_4$
H
O$^+$
Co
BF$_4^-$
OH
254

The cationic 16-electon hydroxyallyl intermediate **252** should receive very little stabilization from the weakly coordinating tetrafluoroborate ion and dichloromethane solvent; as such, **252** is expected to be a very strong Lewis acid. Upon formation of cyclopentadienyl cation **253**, complex **252** could readily accept the newly-formed hydroxyl group as a ligand, thereby activating this ligand for subsequent heterolytic C-O bond cleavage. Such a bond cleavage would produce the 18-electron dicationic Cp*Co(III) cycloheptatriene intermediate **255**, as well as the neutral 18-electron Cp*Co(III) hydroxyallyl hydroxide species **256**; the latter complex should reductively eliminate a molecule of water to afford the Cp*Co(I) acrolein complex **241**, from which **252** had been previously generated.

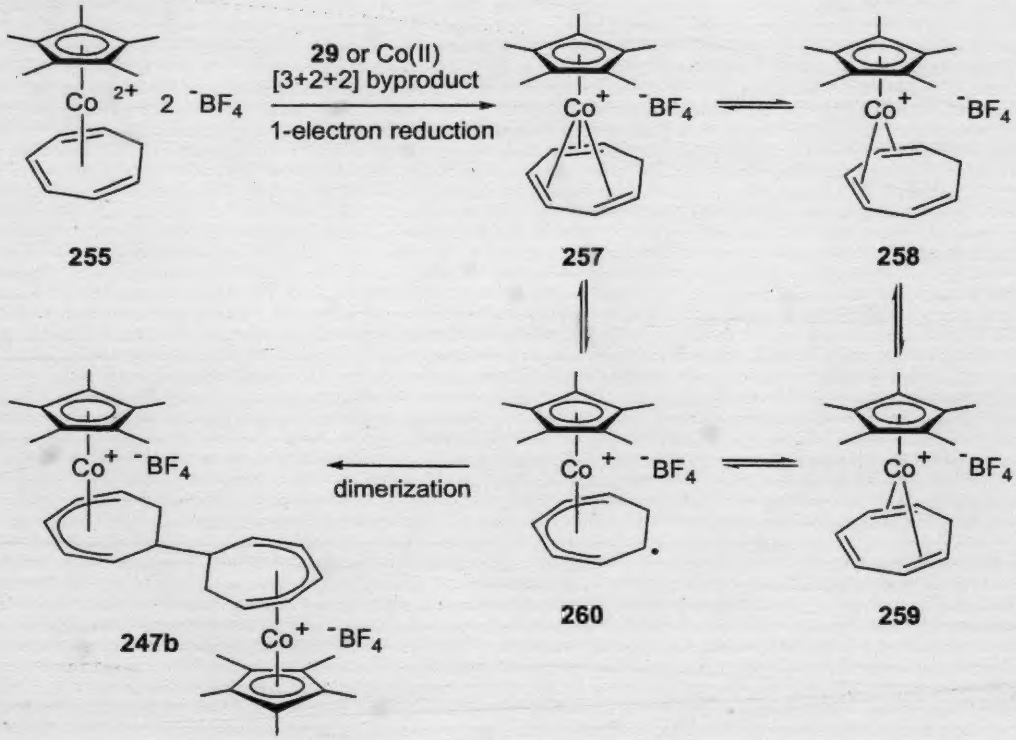
As an alternative to functioning as a Lewis acid, complex **252** might instead behave as a simple Brönsted acid, protonating intermediate **253** at the hydroxyl group, thereby activating this group for elimination as a molecule of water. This alternative also leads to equimolar amounts of dication **255** and, presumably, acrolein complex **241**.

Despite being a formally 18-electron species, the putative dicationic intermediate **255** could then accept a single electron from the Cp*Co(I) complex **241** or, perhaps, from another reductant; cobalt-mediated [3+2+2] cycloadditions often generate small amounts of Co(II) byproducts which might be capable of providing a single electron for the reduction of **255**. Related 18-electron dications are well known; the $Cp^*Co(MeCN)_3^{2+}$ complex, for example, has been isolated by Dzwiniel as the recovered metal template from the oxidative decomplexation of Cp*Co(I) cycloheptadiene complexes (*vide supra*, Chapter 2).

Regardless of the source of the single-electron, reduction of **255** produces the interesting cationic 19-electron Co(II) intermediate **257** which may equilibrate with the 17-electron Co(II) complexes **258** or **259**, and also with the Co(III) ligand-centered stabilized radical complex **260**. Whatever the true nature of the organometallic radical intermediate (**257**, **258**, **259**, or **260**), a ligand-centered radical-coupling step generates the dimeric dication **247b**, which is isolated as **247** after counterion exchange.

Although none of the desired product **253** was isolated from this reaction and very little seven-membered ring-containing product **247** was recovered, this initial trial was encouraging since the presence of **247** indicates that the hydroxyallyl ligand might, in fact, tolerate [3+2+2] cycloaddition reactions. The low yield might be a result of divergent reactivity of cycloheptadienyl complex **253** with the Lewis acidic complexes present. With this is mind, an investigation of the chemistry of the closely related Cp*Co(III) silyloxyallyl complexes was undertaken.

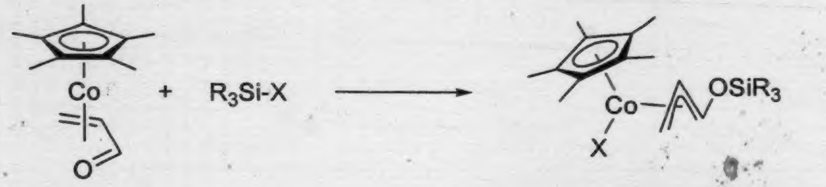
Scheme 3.5


Co 2+
2 ⁻BF4
29 or Co(II)
[3+2+2] byproduct
1-electron reduction
Co+ ⁻BF4
Co+ ⁻BF4
255
257
258
Co+ ⁻BF4
dimerization
Co + ⁻BF4
Co+ ⁻BF4
260
259
Co+ ⁻BF4
247b

*Part C: Synthesis and Characterization of Cp*Co(III) Silyloxyallyl Complexes*

Since Cp*Co(III) hydroxyallyl complexes were not productive precursors to the formation of seven-membered oxygen-bearing carbocycles, it was necessary to consider the use of a protecting group to mask the hydroxy functionality. Among the numerous protecting groups available for the hydroxy group, silyl ethers seemed the most promising for several reasons. Firstly, 1-silyloxyallyl complexes of several transition metals, including cobalt, were known to be stable and could likely be accessed directly from the Cp*Co(I) acrolein complex **241**. Additionally, silyl protecting groups were known to be tolerant of a wide range of chemical conditions; the [3+2+2] cyclization in particular demanded a protecting group resistant to Lewis acid. A related consideration was the recognition that the protecting group could not itself possess appreciable Lewis basicity. One concern with protecting the hydroxy functionality as an ester or ether was the expectation that such a functional group might interfere with normal [3+2+2] chemistry by blocking the required alkyne coordination site, especially if the allyl were to adopt an *anti* stereochemistry. It was also important that a protecting group be chosen such that it could be readily removed from the product complex under conditions otherwise tolerated by that molecule.

Cp*Co(III) 1-(trimethylsilyloxy)allyl chloride **261** was readily synthesized from acrolein complex **241** upon treatment with chlorotrimethylsilane in ether (Equation **3.12**). Although the silyl chloride was added at -78 °C, no colour change was observed until the reaction was warmed to room temperature. The crude product from the reaction was quite clean and deep purple crystals of **261** could be obtained from a pentane/ether solution cooled overnight at -40 °C.



(Eq. 3.12)

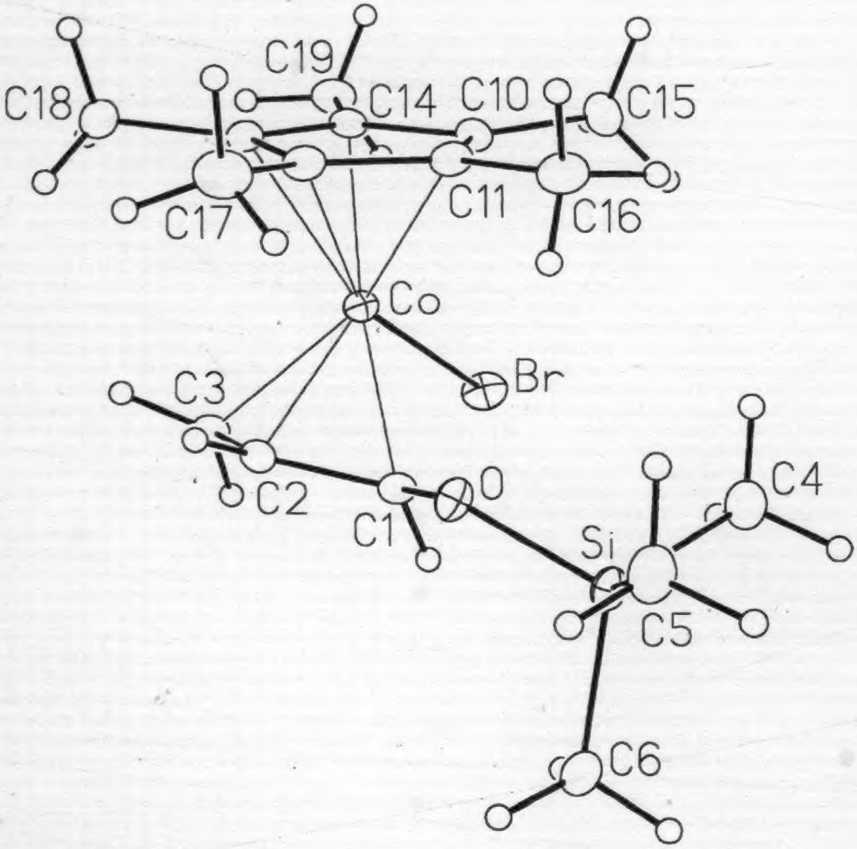
241

261: X = Cl, R = Me, 81%
262: X = Br, R = Me, 83%
263: X = I, R = *i*-Pr, 81%

In a similar fashion, the 1-(trimethylsilyloxy)allyl bromide complex **262** was prepared from bromotrimethylsilane, although the reaction appeared to be complete in seconds at -78 °C. As with **261**, deep purple crystals were obtained by cooling a pentane/ether solution of **262** to -40 °C overnight. In the case of **262**, the crystals were suitable for X-ray crystallographic study; the ORTEP for this complex is depicted in Figure **3.6**.

A silyloxyallyl compound with a more acid-stable protecting group was also desirable, as trimethylsilyloxy ethers are known to be quite acid-sensitive, to the extent that silica gel chromatography is normally sufficient for the deprotection of this group. Acrolein complex **241**, however, was found to be unreactive towards the very bulky silylating agent, chlorotri-*iso*-propylsilane, even upon mild heating and extended reaction times. On the other hand, Cp*Co(III) tri-*iso*-propylsilyloxyallyl iodide **263** was obtained in good yield by reaction of **241** with iodo-tri-*iso*-propylsilane, which was generated *in situ* from sodium iodide and the corresponding silyl chloride in acetone. The organometallic iodide **263** was purified with excellent recovery by crystallization from pentane, although crystals suitable for X-Ray diffraction studies were not obtained.

Figure 3.6: ORTEP for Complex **262** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0327



Final Residuals: R_1 = 0.0359; wR_2 = 0.0850. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Br-Co, 2.4401(5); Co-C1, 2.129(3); Co-C2, 2.018(3); Co-C3, 2.045(3); C1-C2, 1.401(4); C2-C3, 1.415(4).

Selected Torsional Angle (deg.): O-C1-C2-C3, 172.4(3)°.

The dihedral angle between the planes defined by C1-C3 and by C10-C14 = 15.6(2)°.

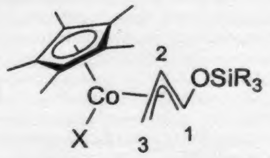
The ^{1}H and ^{13}C NMR spectroscopy of **261**, **262** and **263** is summarized in Tables **3.3** and **3.4**, respectively. In each case, only a single stereoisomer is observed. All three Co(III) halides exhibit a downfield doublet in the ^{1}H NMR spectrum with a coupling constant of approximately 9.0 Hz. The magnitude of the coupling interaction between the central allyl proton and H_3-*syn* is, in each case, about 8.2 Hz whereas the coupling between H_2 and H_3-*anti* is close to 12.4 Hz. Considering that the electron-withdrawing silyloxy group is expected to diminish the coupling interaction between H_1 and H_2, the 9.0 Hz coupling interactions are strong evidence for a *syn* relationship between the silyloxy substituent and H_2.

Table 3.3: ^{1}H NMR Data for Cp*Co(III) Silyloxyallyl Halides **261**, **262**, and **263**

	261	**262**	**263**
H_1 $J_{H1\text{-}H2}$	5.73 (d) 9.1 Hz	6.06 (d) 9.0 Hz	6.09 (dt) 9.1 Hz
H_2 $J_{H2\text{-}H3\mathit{syn}}$	3.74 (dt) 8.2 Hz	3.60 (dt) 8.2 Hz	3.53 (ddd) 8.3 Hz
$H_{3\mathit{syn}}$ $J_{H3\mathit{syn}\text{-}H3\mathit{anti}}$	3.40 (broad d) 0.8 Hz	3.28 (broad d) -	3.28 (ddd) 1.4 Hz
$H_{3\mathit{anti}}$ $J_{H2\text{-}H3\mathit{anti}}$	2.57 (dd) 12.4 Hz	2.80 (broad d) 12.4 Hz	2.69 (ddd) 12.3 Hz
H_{Cp*}	1.31 (s)	1.37 (s)	1.74 (s)
H_R	0.23 (s)	0.23 (s)	1.27 (m, 3H) 1.18 (d, 7.3Hz, 9H) 1.16 (d, 7.3Hz, 9H)

Table 3.4: ^{13}C NMR Data for Cp*Co(III) Silyloxyallyl Halides **261**, **262**, and **263**

	261	**262**	**263**
C_1	111.58	109.23	105.79
C_2	83.18	82.47	81.96
C_3	47.48	45.08	41.42
C_{Cp*}	9.26 (-CH_3) 93.34 (quat.)	9.64 (-CH_3) 93.20 (quat.)	10.73 (-CH_3) 93.47 (quat.)
C_R	-0.44	-0.42	12.41 (-CH-) 18.23 (-CH_3) 18.09 (-CH_3)



261: X = Cl, R = Me
262: X = Br, R = Me
263: X = I, R = *i*-Pr

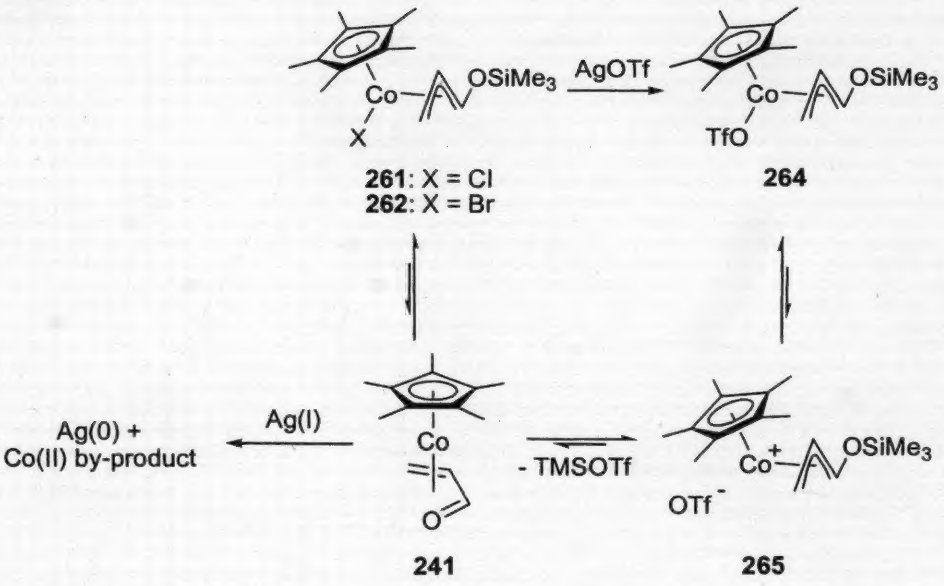
The effect on chemical shift of varying the inner-sphere halide was also apparent, especially in the case of complexes **261** and **262**, where the molecules were otherwise identical. Changing the halide from chloride to bromide had the effect of increasing the chemical shift of the two terminal *anti* protons, while lowering the chemical shift of the central proton as well as the *syn* terminal proton. It is interesting that the two geminal protons H_{3anti} and H_{3syn} were shifted in different directions by replacing chloride with bromide. One possible explanation for this might be related to the size of the inner-sphere halide; substituting chloride with bromide might require the allyl to "slide" across the surface of the metal atom slightly, moving H_2 and H_{3syn} into a region that is slightly more anisotropically shielding while, at the same time, moving H_1 and H_{3anti} into a slightly more deshielding environment.

With several Cp*Co(III) silyloxyallyl halides in hand, the reactivity of these complexes with alkynes was probed, with an eye to generating oxygen-bearing seven-membered ring complexes. Trimethylsilyloxyallyl complexes **261** and **262** were assayed first; treatment of either of these complexes with silver triflate at low temperature in the presence of acetylene resulted only in the immediate formation of a green colour, as well as a black precipitate.

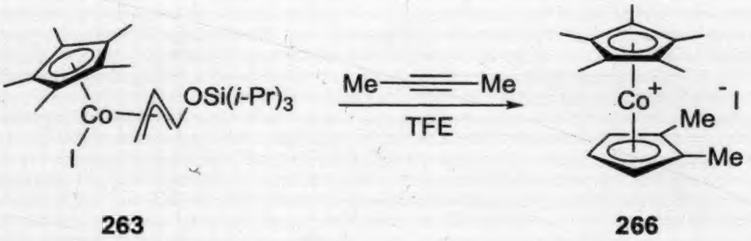
While no additional evidence was gathered to support this speculation, it may be that the silver ion was reduced to metallic Ag(0). While it is unlikely that the electron necessary for this reduction was provided by the Co(III), it is possible that the more strongly reducing Co(I) is generated *in situ* from intermediate **264** which, given the weak coordinating nature of the triflate ion, is expected to exist in equilibrium with **241** via the reactive cationic intermediate **265** (Scheme **3.6**). The Co(I) complex **241** is extremely air sensitive, and as such is certainly capable of reducing Ag(I) to Ag(0), forming green Co(II) in the process. It is also possible that **241** forms directly from **261** or **262** by direct action of silver triflate on the inner-sphere halide complex.

Attempts to generate tractable seven-membered ring products by reaction of **261** and **262** with acetylene in acetone in the presence of KPF_6 also proved fruitless. As well, dissolution of **262** in the ionizing solvent 2,2,2-trifluoroethanol under a stream of acetylene failed to yield identifiable products.

Scheme 3.6

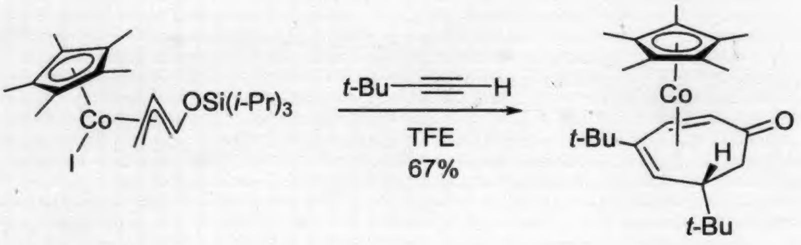

OSiMe3
AgOTf
Co
X
OSiMe3
Co
TfO
261: X = Cl
262: X = Br
264
Ag(0) +
Co(II) by-product
Ag(I)
Co
O
- TMSOTf
Co+
OSiMe3
OTf-
241
265

Tri-iso-propylsilyloxyallyl complex **263** also failed to furnish isolable and identifiable products upon reaction with acetylene in acetone or 2,2,2-trifluoroethanol. However, when a 2,2,2-trifluoroethanol solution of **263** was treated with 2-butyne, the red-purple solution became yellow-green almost instantly and cobaltacinium complex **266** was obtained exclusively in good yield after silica gel chromatography (Equation **3.13**).


Co
I
OSi(i-Pr)3
Me——Me
TFE
Co+
-I
Me
Me
263
266

(Eq. 3.13)

More interestingly, the iodide complex **263** reacted instantly with *t*-butylacetylene in 2,2,2-trifluoroethanol, as evidenced by a rapid colour change to a green-brown. Removal of the solvent *in vacuo*, followed by silica gel chromatography, afforded a purple solid which was further purified in 67% overall yield by crystallization from pentane at -80 °C. Spectroscopic interrogation of the purple compound, coupled with X-ray crystallographic analysis, identified the product as Cp*Co (cycloheptadienone) **267**.

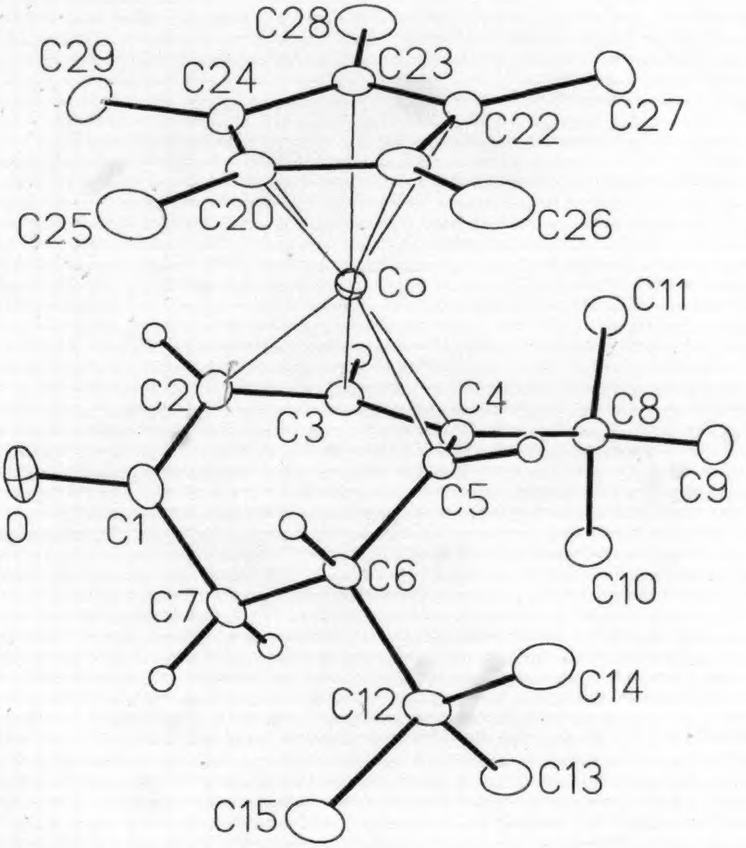


263 **267**

(Eq. 3.14)

Although **267** is most conveniently formalized as Co(I), it is indefinitely air- and moisture-stable, both as a solid and in solution. Furthermore, the complex is resistant to photolytic oxidative decomplexation with allyl bromide. This unusual air-stability can in part be attributed to the conjugated electron-withdrawing carbonyl group; the infra-red spectrum shows a carbonyl stretching absorption at 1612 cm^{-1}, indicating significant electron donation into this carbonyl group. Only a few alkyl-substituted cycloheptadienones are known, and relevant carbonyl stretching frequencies are listed in Table **3.5**.[169] The effect of coordination to the Cp*Co(I) template appears to be a shift of about 40 wavenumbers, reflecting the electron-donating nature of the cobalt template.

Figure 3.7: ORTEP for Complex **267** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0337


C28
C29
C24
C23
C27
C22
C20
C25
C26
Co
C11
C2
C3
C4
C8
C9
O
C1
C5
C6
C10
C7
C14
C12
C13
C15

Final Residuals: $R_1 = 0.0313$; $wR_2 = 0.0944$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

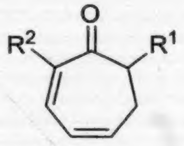
Selected Bond Distances (Å): O-C1, 1.233(2); C1-C2, 1.445(3); C1-C7, 1.506(3); C2-C3, 1.427(3); C3-C4, 1.421(2); C4-C5, 1.445(2); C5-C6, 1.529(2); C6-C7, 1.530(3).

Selected Torsional Angle (deg.): O-C1-C2-C3, -174.97(19)°.

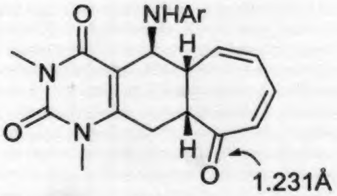
The dihedral angle between the planes defined by C2-C5 and by C20-C24 = 20.95(11)°.

Table 3.5: Carbonyl Stretching Frequencies from Several Cycloheptadienones

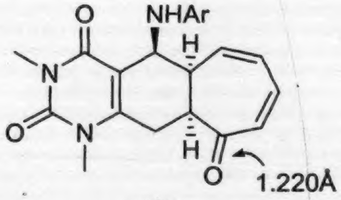
R^1	R^2	ν_{CO} (cm^{-1})
H	H	1660
Me	H	1653
H	Me	1655



It is noteworthy that the solid-state carbonyl C-O bond length from the X-Ray crystal structure is 1.233(2) Å, a value not significantly different than the carbonyl bond lengths reported for organic cycloheptadienones **268** and **269**, the only non-coordinated 2,4-cycloheptadienones for which X-ray structural data is available.[170]



268



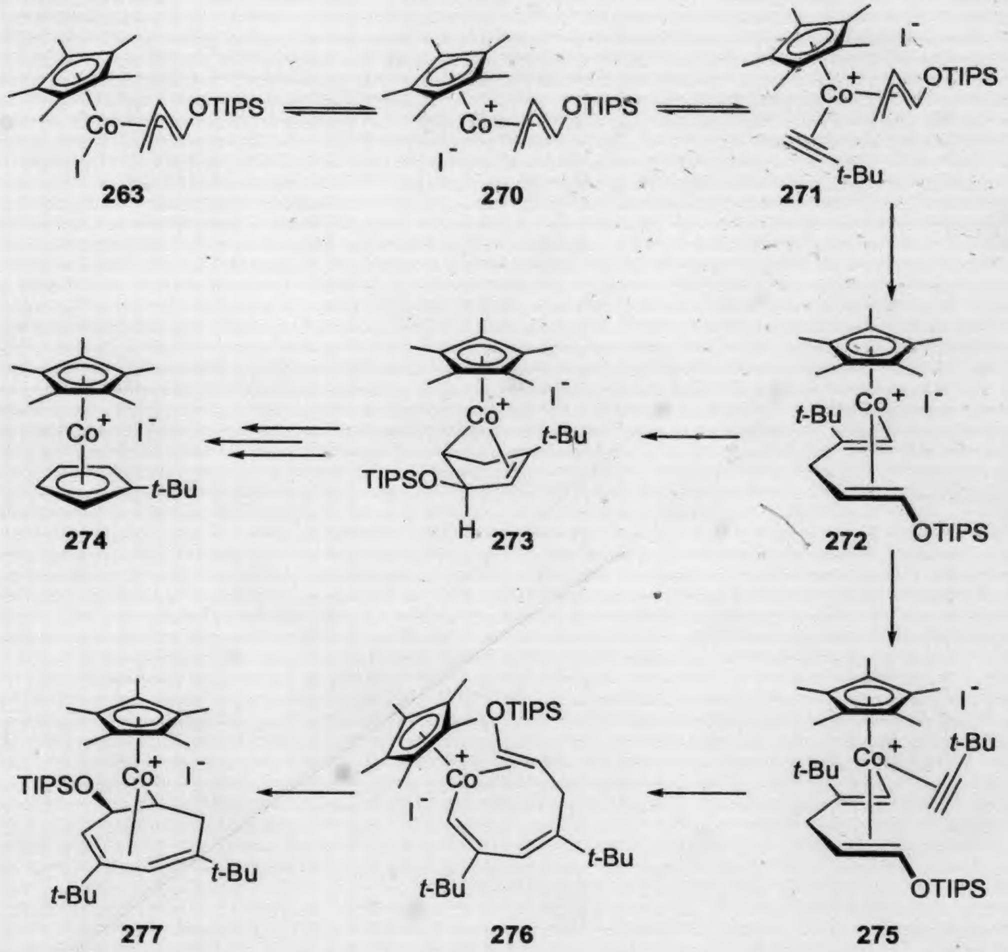
269

Ar = p-Br-C_6H_4

Because the initial crude product from the reaction between **241** and *t*-butyl acetylene was a green-brown colour, whereas the chromatographed final product **267** was deep purple, it appears that the silica gel chromatography was not chemically innocent, and was instead responsible for the ultimate generation of Co(I) complex **267**. In fact, ^{1}H NMR analysis of the crude *unchromatographed* product revealed that complex **267** was entirely absent. Attempts to isolate and purify the presumably Co(III) intermediate met with frustration, but some clues to the identity of the green-brown intermediate were gleaned from the ^{1}H NMR and GCOSY spectroscopy.

The mechanism for the formation of cycloheptadienone **267** most likely involves a number of steps that parallel those proposed for the normal [3+2+2] cycloaddition process (Scheme **3.7**). In the initial step, the 18-electron silyloxyallyl iodide must generate a coordination site. One possibility is that the iodide simply dissociates to form

Scheme 3.7

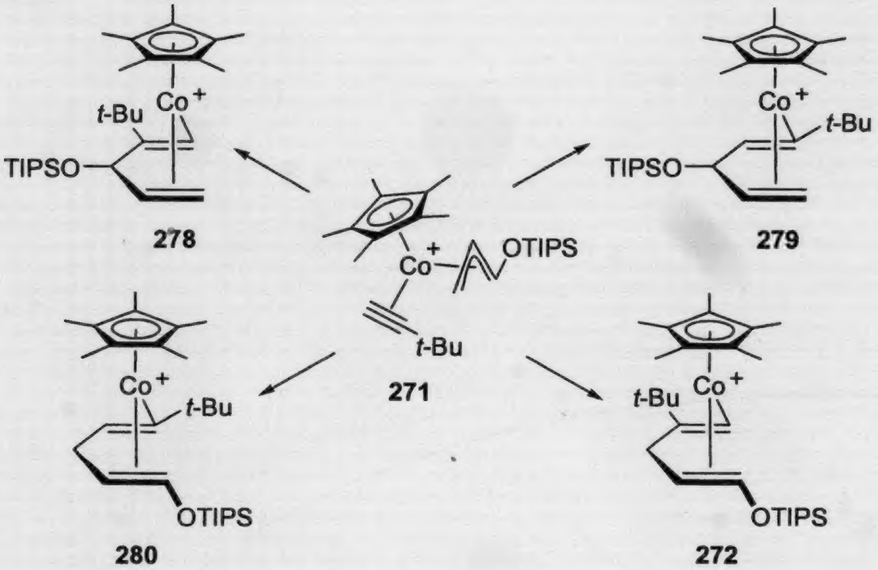


Co
OTIPS
I
263
Co+
OTIPS
I-
270
I-
Co+
OTIPS
t-Bu
271
t-Bu
Co+
I-
OTIPS
272
Co+
I-
t-Bu
TIPSO
H
273
Co+
I-
t-Bu
274
I-
t-Bu
Co+
t-Bu
OTIPS
275
OTIPS
Co+
I-
t-Bu
t-Bu
276
TIPSO
Co+
I-
t-Bu
t-Bu
277

outer-sphere complex **270**, which should enjoy significant stabilization from the 2,2,2-trifluoroethanol solvent. Subsequent coordination of the alkyne then generates cationic complex **271**; such allyl alkyne complexes have been proposed previously as intermediates in [3+2+2] reactions.

In principle, the migratory insertion of the alkyne into the allyl-metal bond could proceed from **271** to afford four possible intermediates (Scheme **3.7**, additional details shown in Scheme **3.8**). The alkyne could react to form a carbon-carbon bond at either end of the alkyne unit. As well, the unsymmetrical allyl fragment may migrate to form a new carbon-carbon bond at either terminus.

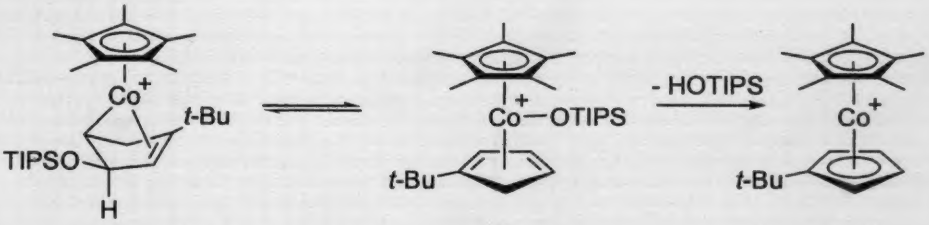
Scheme 3.8



Inspection of the product structure reveals that, assuming that the mechanism does not involve any subsequent C-C or C-O activation steps, two of the four possible insertion geometries, **278** and **280**, may be dismissed, as they cannot lead to the 1,3,5 substitution pattern found in the isolated product. Of the remaining insertion geometries, complex **272** might be considered the most reasonable: it places the bulky *t*-butyl group away from the hindered metal center, and migration to form intermediate **272** involves bond formation at the least hindered terminus of the allyl moiety. Insertion product **279**, however, cannot be entirely dismissed as a viable intermediate.

From complex **272** (or **279**), the reaction can diverge. If binding and insertion of the second equivalent of alkyne is inhibited, intermediate **272** can cyclize to form the cationic η^1,η^2-cyclopentenyl complex **273**, which in turn generates cobaltacinium complex **274** (Scheme **3.9**). On the other hand, if cyclization is slow and a sufficient concentration of alkyne is present, a second equivalent can bond to coordinatively unsaturated **272** to afford the 18-electron intermediate **275** (Scheme **3.7**). The regioselectivity of the second alkyne insertion may also be directed by the steric bulk of the *t*-butyl group and the metal center.

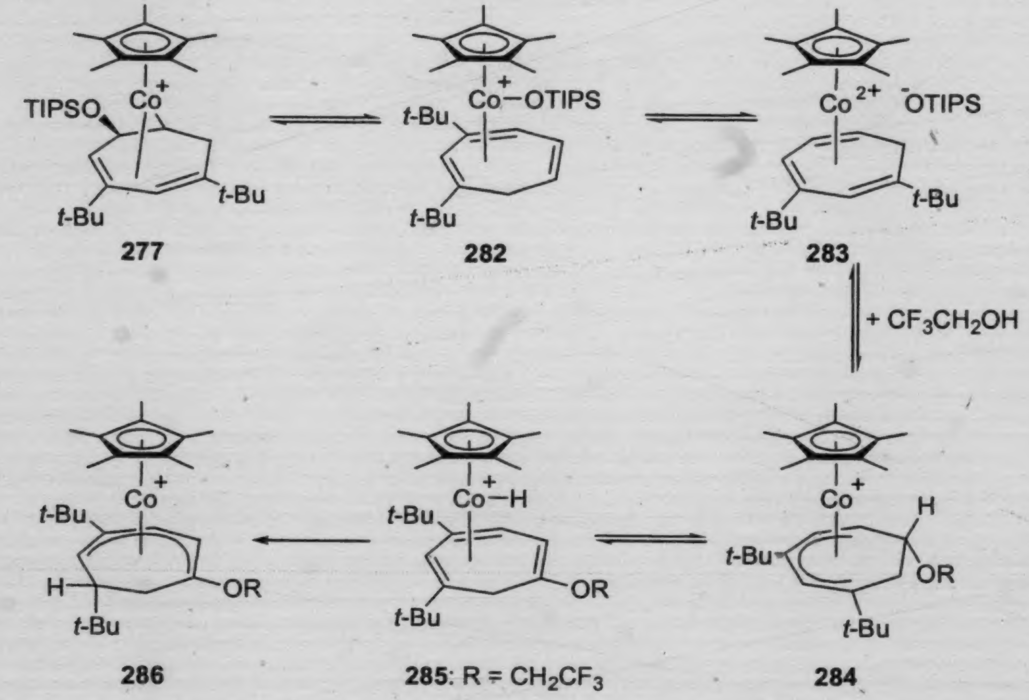
Scheme 3.9



273 **281** **274**

Subsequent ring closure of **276** affords the η^1,η^4-intermediate **277**, which is similar to intermediates that have been previously postulated in the normal [3+2+2] process (i.e. **99**, Scheme **2.11**). Complex **277** differs from previous examples, however, in that it possesses an activated C-O bond in the position β to the carbon-metal σ-bond. Scission of this bond leads either to triene intermediate **282** in which the triene unit is η^4-bound to the metal or directly to the dicationic η^6-cycloheptatriene complex **283**; the latter possibility is more likely given the bulk of the OTIPS ligand. In 2,2,2-trifluoroethanol solvent, **283** could then rapidly and reversibly add 2,2,2-trifluoroethoxide to the *exo* face of the electrophilic triene ligand. It is noteworthy that complex **283** is structurally related to the dicationic complex **255**, which was proposed as a reactive intermediate in the formation of the dimeric complex **247** (Scheme **3.5**).

Scheme 3.10


TIPSO
Co+
t-Bu
t-Bu
277
Co+–OTIPS
t-Bu
t-Bu
282
Co2+
-OTIPS
t-Bu
t-Bu
283
+ CF3CH2OH
Co+
t-Bu
t-Bu
H
OR
286
Co+–H
t-Bu
t-Bu
OR
285: R = CH2CF3
Co+
H
t-Bu
OR
t-Bu
284

Of the several possible 2,2,2-trifluoroethoxide adducts accessible from triene complex **283**, cycloheptadienyl complex **284** should be thermodynamically preferred, the result of nucleophilic addition to the unsubstituted terminus of the triene unit; addition to the other terminus creates a sterically unfavourable quaternary center adjacent to the *t*-butyl group.

Complex **284** is the first compound in the proposed sequence that might reasonably be expected to be isolable and, as such, represents a candidate structure for the green-brown intermediate that converts to **267** upon silica gel chromatography in the presence of methanol. However, complex **284** is not consistent with the ^{1}H NMR data from the unidentified intermediate; a far more likely candidate for this intermediate is complex **286** (Scheme **3.10**), which is accessible from complex **284** via β-hydride elimination and subsequent reinsertion at the *t*-butyl-bearing terminus. There is, however, no definitive prior example of such a β-hydride elimination from any Cp*Co(III) cycloheptadienyl complex, although intermediate **284** is the first example of such a compound with a heteroatom substituent adjacent to the pentadienyl fragment. It may be that the lone pair from the 2,2,2-trifluoroethoxy group is capable of lowering the energy barrier to β-hydride activation by interacting with the anti-bonding C-H LUMO in the transition state for β-hydride elimination.

The NMR data for the ring protons of the green pre-chromatography intermediate, tentatively assigned as cycloheptadienyl complex **286**, are summarized in Table **3.6**. Notably absent from the ^{1}H NMR spectrum is any evidence for the presence a TIPS group. A quartet at 3.99 ppm indicates a single 2,2,2-trifluoroethoxy moiety. The only other characterization data that was obtained for this intermediate was a GCOSY spectrum, which revealed several informative correlations. The broad singlet appearing at 3.71 ppm exhibits weak coupling to signals at 6.01, 3.00, and 2.49 ppm, reflecting the cyclic nature of the postulated complex **286**.

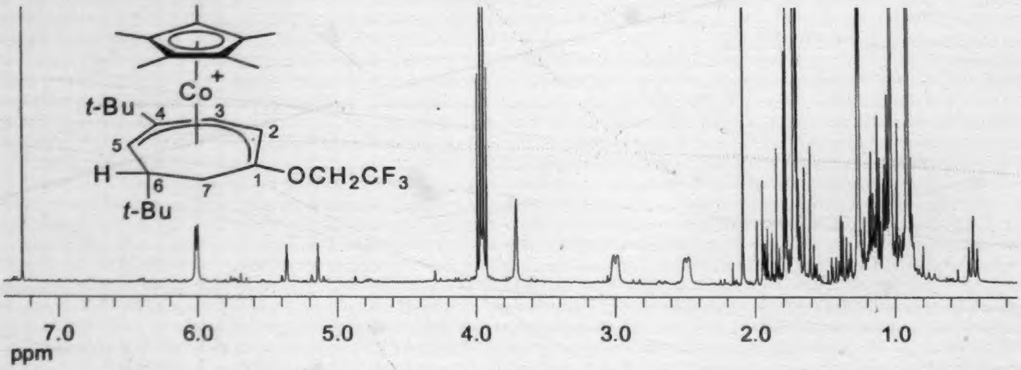
One other item of note in the ^{1}H NMR spectrum of the crude reaction intermediate is the presence of a pair of mutually coupled triplets at 5.36 ppm and 5.14 ppm (J = 1.9 Hz). These multiplets, which are not attributable to **286**, indicate the competitive formation of a small amount of the cobalticinium complex **274**; the formation of complex **274** is not surprising given that cobalticinium formation is the dominant pathway when 2-butyne is used for the cycloaddition reaction. Based on the ^{1}H NMR integration, approximately 10 – 15% of the Co(III) silyloxyallyl iodide is converted to cobalticinium, which in part accounts for the less than quantitative yield of **267**. All attempts to purify the intermediate by direct crystallization failed; silica gel chromatography resulted only in the formation of isolable product **267**.

Table 3.6: Summarized ^{1}H Data for **286**

	H_2	H_3	H_5	H_6	H_{7exo}	H_{7endo}
δ (ppm)	3.94[a]	6.01 (d)	3.71 (br s)	3.00 (br d)	0.44 (t)	2.49 (br d)
J (Hz)	-	6.0	-	11.9	11.9	11.9

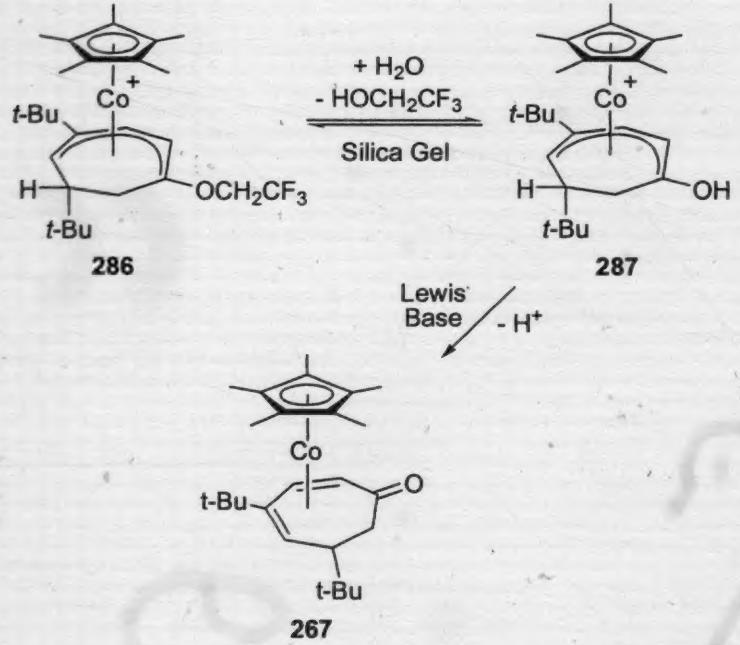
[a] The signal arising from H_2 of **286** at 3.94 ppm (as evidenced by an observed correlation in the COSY spectrum) is obscured by the more intense 2,2,2-trifluoroethoxy methylene quartet at this chemical shift.

Figure 3.8: ^{1}H NMR Spectrum of Crude **286**



Assuming that the identity of the labile intermediate is indeed complex **286**, the mechanism for the conversion to cycloheptadiene complex **267** may simply involve

Scheme 3.11


Co+
t-Bu
H
OCH₂CF₃
t-Bu
286
+ H₂O
- HOCH₂CF₃
Silica Gel
Co+
t-Bu
H
OH
t-Bu
287
Lewis Base
- H+
Co
t-Bu
O
t-Bu
267

nucleophilic attack of water on the methylene group of the 2,2,2-trifluoroethoxide moiety to generate complex **267**. It is noteworthy that application of the crude intermediate **286** to the silica gel column using pure dichloromethane does not immediately result in a colour change, the purple colour is only observed when methanol is added to the eluent. Intermediate **287** has not been observed; the cationic nature of the metal center should render the hydroxyl proton very acidic and thus conversion to **267** from **287** requires only a weakly basic species such as methanol or water.

Part D: Summary and Outlook

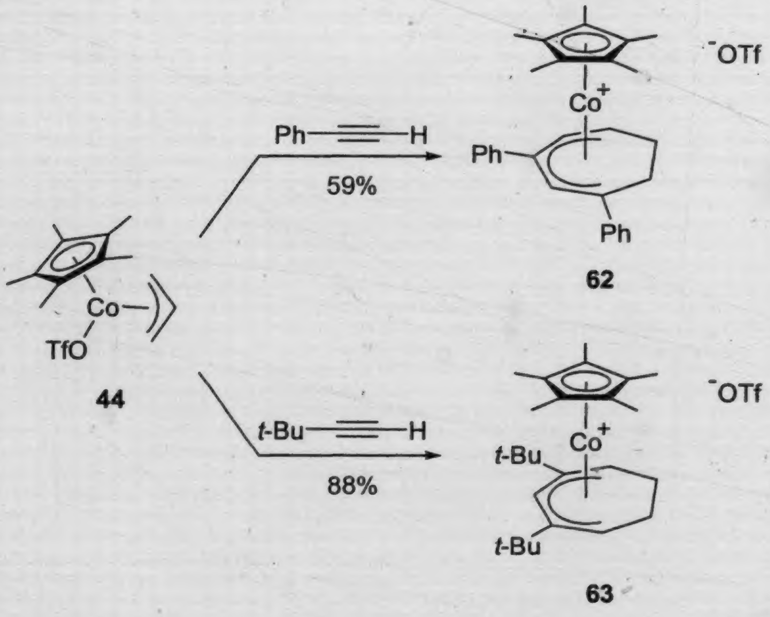
At present, the cycloheptadienyl complex **267** remains the only example of an oxygen-bearing seven-membered ring product obtained from a cobalt-mediated [3+2+2] cycloaddition of an oxyallyl complex. Because our attempts to incorporate another alkyne, including acetylene, phenylacetylene, trimethylsilylacetylene, and 2-butyne, failed to furnish seven-membered ring products, the successful incorporation of *t*-butylacetylene must be regarded as anomalous; as such, the synthetic utility of the process is of questionable scope.

The unusual reactivity of *t*-butylacetylene may arise from the mechanistic role that the bulky *t*-butyl group plays in directing the reaction of this alkyne (and only this alkyne) to afford the seven-membered ring product. It may be that, of all of the alkynes employed in this study, *t*-butylacetylene is the lone example of a "normal" alkyne; the others may each have failed as a result of steric and/or electronic influences absent in a simple monoalkyl alkyne.

The reaction of **263** with 2-butyne yielded only cobalticinium **267** in good yield (Equation **3.13**). Presumably, coordination and insertion of a second equivalent of the disubstituted alkyne is sterically inhibited: 2-butyne was the first alkyne for which the "anomalous" [3+2+2] cycloaddition was observed by Etkin[101] (Scheme **2.4**) and, more recently, by Dzwiniel.[17,101] Dzwiniel too proposes that the carbon-carbon activation pathway preceeds coordination and insertion of a second equivalent of 2-butyne into the putative vinyl olefin (Scheme **2.11**) intermediate is sterically inhibited.

Phenylacetylene, however, also fails to furnish seven-membered rings upon reaction with silyloxyallyl complex **263**; an intractable mess containing a small amount of the corresponding cobalticinium complex was obtained instead. Dzwiniel[17] previously used phenylacetylene in [3+2+2] cycloadditions (Scheme **3.12**) with Co(III) allyl

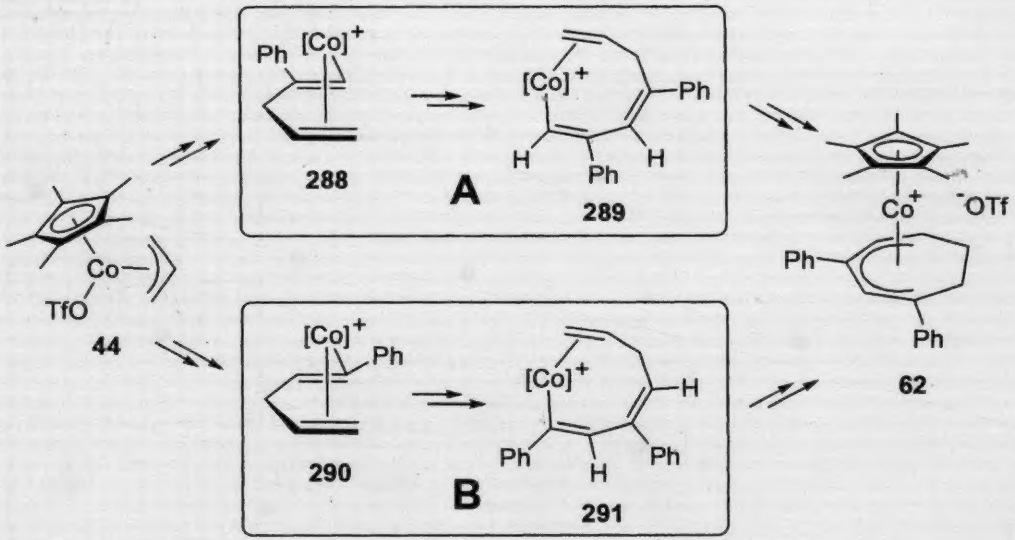
Scheme 3.12



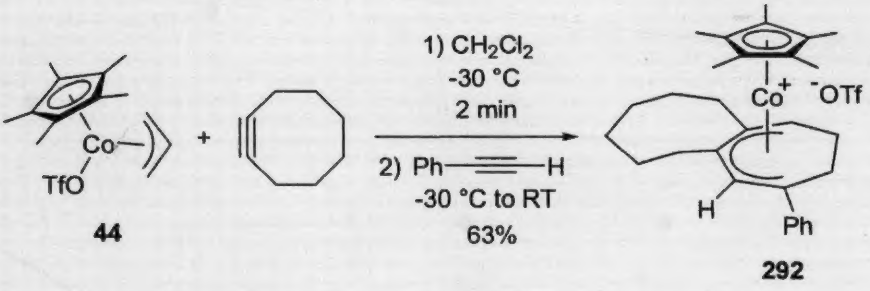
complexes, finding that this alkyne behaves differently from other terminal alkynes with respect to the regiochemistry of the cycloaddition process. The reaction of phenylacetylene with complex **44** furnishes the 1,3-diphenylcycloheptadienyl complex **62** in 59% yield; the reaction of with *t*-butylacetylene affords 2,5-di-*tert*-butyl complex **63** as the only isolated seven-membered ring product. Barring a very unusual carbon-carbon activation process, this indicates that the two alkynes insert with different regiochemical preferences.

Dzwiniel[17] suggested that the proposed vinyl olefin intermediate should normally form with substituents preferentially placed in the β-position, as α-substitution on such vinyl fragments would be sterically unfavourable, except in the case of overriding electronic effects. In the case of a phenyl substituent, it is not immediately clear which insertion geometry should be favoured, since the sterically imposing phenyl group could electronically stabilize the vinyl metal-carbon bond if placed in the α-position. Indeed, Dzwiniel identified two possible pathways for the formation of product **62** (Scheme **3.13**). In both pathways, the relative regiochemistry of the two phenyl substituents is realized by a mutual "head-to-tail" insertion of the phenylacetylene fragments. In one pathway, however, both alkyne insertions proceed to place the phenyl group β to the metal; in the other pathway, each insertion places the incoming phenyl group in the α-position.

Scheme 3.13



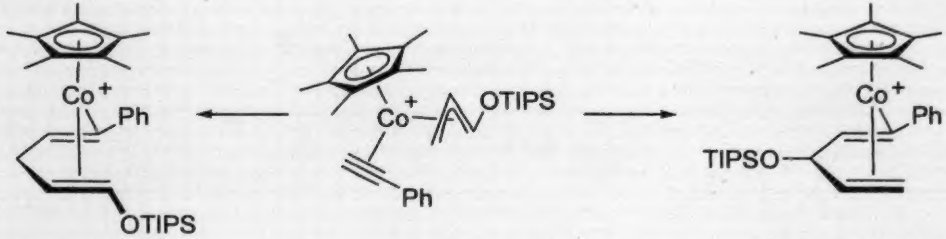
Since both pathways A and B converge to a common intermediate in the formation of cycloheptadienyl complex **62**, it was not immediately clear which pathway was preferred. However, evidence for the prevalence of pathway A was uncovered by Dzwiniel in a related *mixed* [3+2+2] reaction, which incorporated one equivalent each of cyclooctyne and phenylacetylene into a single cycloheptadienyl complex **292**. Mixed [3+2+2] reactions typically fail to yield a single product, since most such Cp*Co(III) allyl alkyne cations dissociate and reassociate the alkyne at a rate much faster than the subsequent insertion step. The reaction with cyclooctyne (Equation **3.15**) represents a rare exception to this behavior, as the cyclooctyne-coordinated intermediate is resistant to alkyne exchange owing to the elevated π-acidity of the strained cyclooctyne ligand.



(Eq. 3.15)

Barring an unusual carbon-carbon bond activation process, the position of the phenyl group in complex **292** can only be realized if the second alkyne insertion step proceeds to place the phenyl group in the position α to the cobalt. As such, phenylacetylene is thus also unusual among the alkynes investigated by Dzwiniel. Dzwiniel never attempted a cycloaddition of phenylacetylene with a Cp*Co(III) allyl complex bearing a substituent and, as such, no direct comparison can be drawn between Dzwiniel's reaction and the attempted cycloaddition of phenylacetylene with silyloxyallyl complex **263**. However, if the initial migratory insertion of putative intermediate **293** proceeds to an intermediate bearing the phenyl group in an α-position, only two possibilites arise: regioisomeric intermediates **294** and **295** (Scheme **3.14**). Of these, the formation of isomer **294** might be inhibited by the sterically unfavourable formation of a new carbon-carbon bond at the already-substituted allyl terminus. On the other hand, the formation of intermediate **295** could be non-productive for seven-membered ring formation because of the bulky substituents at either end of the five-carbon framework, inhibiting subsequent bond formation or, perhaps, precluding coordination of the second alkyne.

Scheme 3.14



295 **293** **294**

Trimethylsilylacetylene was not employed by Dzwiniel as a component in [3+2+2] cycloaddition chemistry. However, it is quite likely that the initial migratory insertion chemistry of this alkyne is similar to that of phenylacetylene, as the trimethylsilyl group is also capable of stablizing a carbon-metal bond in the α-position; this effect may overwhelm the competing steric drive to place this bulky group in the β-position. As such, the failure of trimethylsilyl acetylene to afford a seven-membered ring product might be rationalized in a similar manner to the phenylacetylene case.

The failure of the parent alkyne, acetylene, to furnish a cycloaddition product might be the most easily rationalized of all of the negative results. Although Dzwiniel employed trifluoroethanol as an ionizing solvent in a number of reactions, he never reported using this solvent in reactions using acetylene. The very low solubility of acetylene in trifluoroethanol may thus be the primary reason that no seven-membered ring was isolated from our attempted cycloadditions using acetylene.

It is apparent that the reactivity of silyloxyallyl complex **263** with alkynes needs to be re-addressed using a wider selection of monosubstituted alkynes to determine whether the observed reactivity of *t*-butylacetylene is indeed unique. Additionally, the use of an electron-rich alkyne such as ethoxyacetylene remains to be investigated.

Chapter 4 – Seven-Membered Carbocycles From a Cobalt-Mediated [5+2] Pentadienyl/Alkyne Cycloaddition

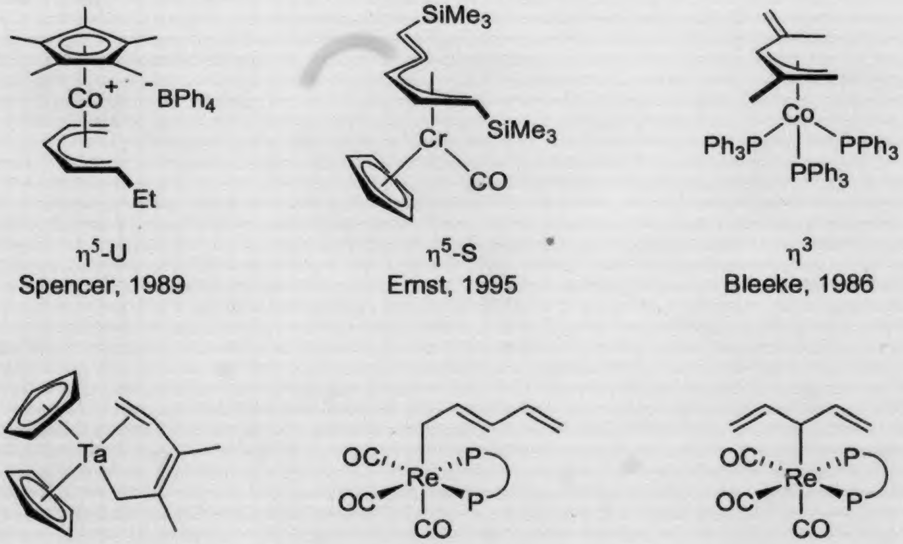
Section 1: Introduction

Part A: Pentadienyl Ligands in Cycloaddition Chemistry

A thorough review of the chemistry of the pentadienyl ligand is available elsewhere[171] and as such is beyond the scope of this thesis. However, some of the fundamental chemistry is summarized here as it is directly relevant to the synthesis of Cp*Co(III) η^5-pentadienyl complexes, as well as to any efforts to realize cycloaddition chemistry using the complexes to afford seven-membered ring compounds.

Perhaps the most striking characteristic of the acyclic pentadienyl ligand is its ability to adopt a number of different binding modes and, in many cases, access more than one of these binding modes along a given reaction pathway. This flexibility is central to organometallic pentadienyl chemistry and is often exploited to access chemistry not available to cyclic analogues, including the ubiquitous cyclopentadienyl ligand, as well as the "interrupted" or "out-of-step" Cp homologues such as the η^5-cyclohexadienyl and η^5-cycloheptadienyl ligands.

Pentadienyl ligands have been observed in η^5-, η^3-, and η^1-binding modes; for each of these three hapticities, at least two well-defined binding modes have been identified (Figure **4.1**). The most common geometry for η^5-pentadienyl coordination is the η^5-U configuration, although an alternative η^5-S configuration has been identified among some metals bearing a d^4 electronic configuration.



η^5-U
Spencer, 1989

η^5-S
Ernst, 1995

η^3
Bleeke, 1986

η^3
Ernst, 1995

η^1
Bleeke, 1989

η^1
Bleeke, 1989

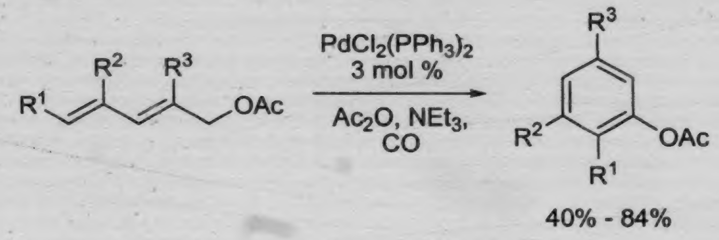
Figure 4.1: Examples of the Various Binding Modes Available to the Pentadienyl Ligand[172-176]

Structurally, the η^5-pentadienyl binding mode has been well characterized in the solid state by X-ray crystallographic study across a range of metals. Barring extreme steric influence, the five pentadienyl carbons are normally coplanar, with attached substitutents bent slightly above this plane toward the metal. This plane is typically closer to the metal than the corresponding plane of an otherwise identical cyclopentadienyl complex; in many cases the pentadienyl ligand is more tightly bound to the metals center while at the same time exhibiting increased reactivity when compared to a closed cyclopentadienyl ligand.[171,177,178]

The most common η^3-pentadienyl binding mode is structurally and chemically very similar to a simple η^3-allyl ligand with an appended vinyl group. This co-ordination mode is often readily accessible from the η^5-U mode by equilibrium dissociation of two carbons. Far less common is an η^3-binding mode in which carbons two and three of the pentadienyl ligand are not bonded to the metal.

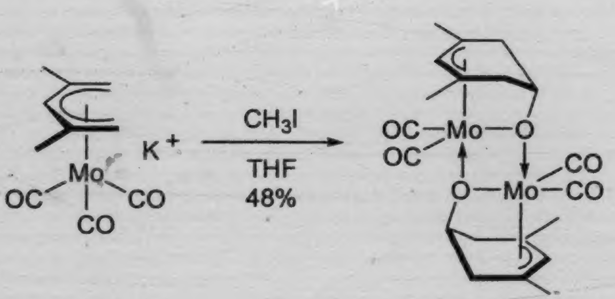
Typically, an η^1-pentadienyl ligand is bound at one terminal carbon as this results in the thermodynamically more stable primary carbon-metal bond as well as a more favorable conjugation of the diene functionality. In some cases, however, the σ-bond exists between the metal and the central carbon of the pentadienyl ligand. In either case, the chemistry accessible to the complex is often similar to that of related σ-alkyl complexes, although the σ-bond is somewhat weaker.

Despite the potentially rich chemistry of the pentadienyl ligand, very few examples exist of the incorporation of this five-carbon unit into a cyclic system via a metal-mediated cycloaddition process. One example of a formal [5+1] cycloaddition was reported in 1991 by Hidai,[179] in which pentadienyl acetates were cyclocarbonylated catalytically by palladium, furnishing phenols in generally moderate yields (Equation **4.1**).


R^1
R^2
R^3
OAc
PdCl2(PPh3)2
3 mol %
Ac2O, NEt3,
CO
R^3
R^2
OAc
R^1
40% - 84%

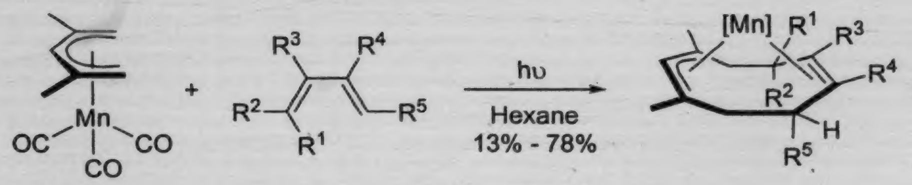
(Eq. 4.1)

Ernst has also described a [5+1] process[180,181] in which a carbonyl ligand is incorporated into a six-membered ring to furnish a dimeric molybdenum complex (Equation **4.2**).


K+
Mo
OC
CO
CO
CH3I
THF
48%
OC—Mo—O
OC
CO
CO
O—Mo—CO

(Eq. 4.2)

In the early 1990's, Kreiter and co-workers described[182-185] a photo-induced [5+4] cycloaddition of dienes and pentadienyl ligands (Equation **4.3**). Yields of cyclononadienyl manganese products **297** were variable, ranging from 13% to 78% depending on the nature of the diene employed. In addition to the 2,4-dimethylpentadienyl manganese complex **296**, the unsubstituted pentadienyl analogue was also employed successfully in some reactions.


R3
R4
+
R2
R5
R1
Mn
OC
CO
CO
hυ
Hexane
13% - 78%
[Mn]
R1
R3
R4
R2
H
R5

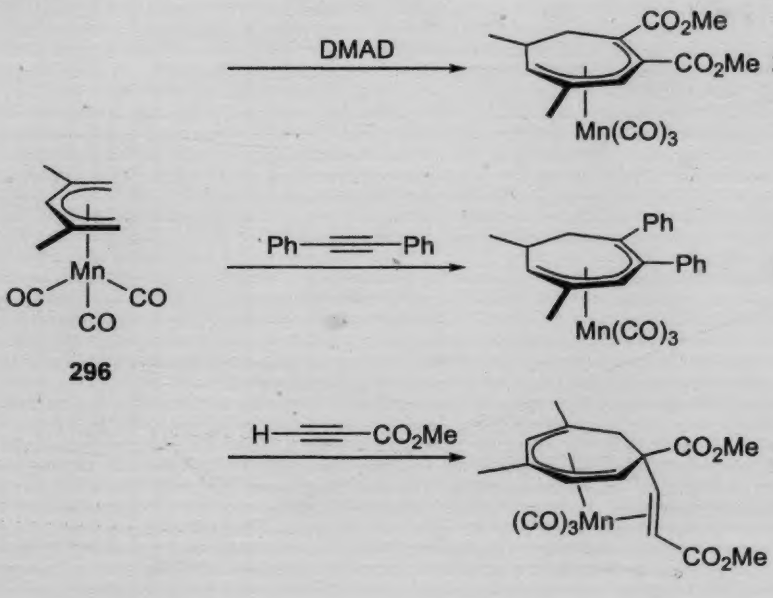
(Eq. 4.3)

296

297: [Mn] = $Mn(CO)_3$

Similar methodology was applied to the incorporation of alkynes into these manganese pentadienyl complexes.[186,187] Dimethylacetylenedicarboxylate and diphenylacetylene were each incorporated, albeit in very low yield, in a photochemical [5+2] process to afford cycloheptadienyl products **298** and **299** (Scheme **4.1**). Contrastingly, two molecules of methyl propionate were incorporated under similar

Scheme 4.1


DMAD
CO2Me
CO2Me
Mn(CO)3
Mn
OC
CO
CO
Ph—≡—Ph
Ph
Ph
Mn(CO)3
H—≡—CO2Me
CO2Me
(CO)3Mn
CO2Me

296

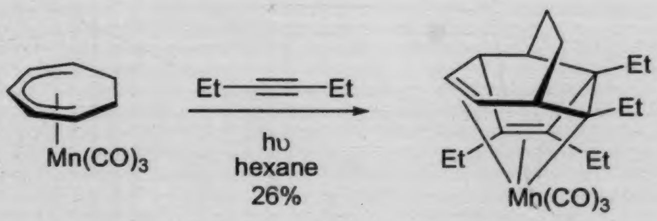
298, 12%

299, 11%

300, 28%

conditions; no simple [5+2] adduct was observed for this alkyne, although the double-insertion product **300** was isolated.

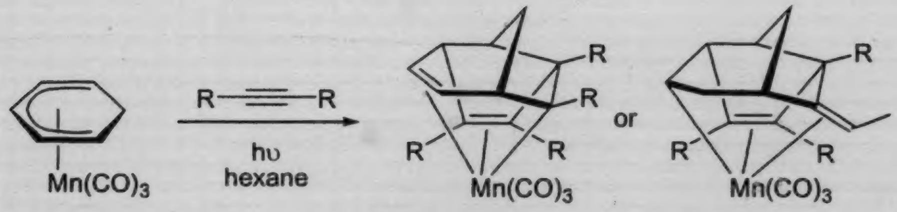
More recently, Kreiter has focused on the use of cyclic, or closed, pentadienyl ligands in cycloadditions with alkynes. Cycloheptadienyl complex **301** incorporates two equivalents of 3-hexyne[188] in a [5+2], *homo*[5+2] tandem process which furnishes the tricyclic manganese complex **302** in 26% yield (Equation **4.4**).



(Eq. 4.4)

301 **302**

Cyclohexadienyl homologue[189,190] **303** incorporates 2-butyne and diphenylacetylene in a similar fashion, but upon reaction with 3-hexyne proceeds further to the rearranged complex **306** (Equation **4.5**). In no case was Kreiter able to isolate a simple [5+2] monoadduct.



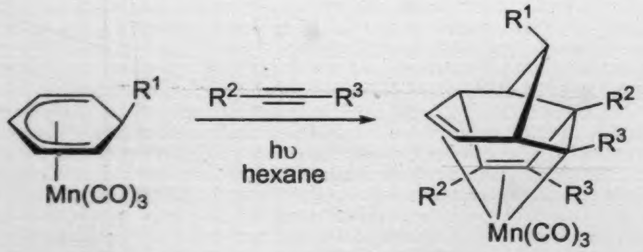
(Eq. 4.5)

303

304: R = Me, 28%
305: R = Ph, 30%

306: R = Et, 28%

At about the same time, Sheridan[191] was also investigating this photochemical cycloaddition reaction. Similar conditions were employed by Sheridan, although much better yields of tricyclic products were obtained (Equation **4.6**).



(Eq. 4.6)

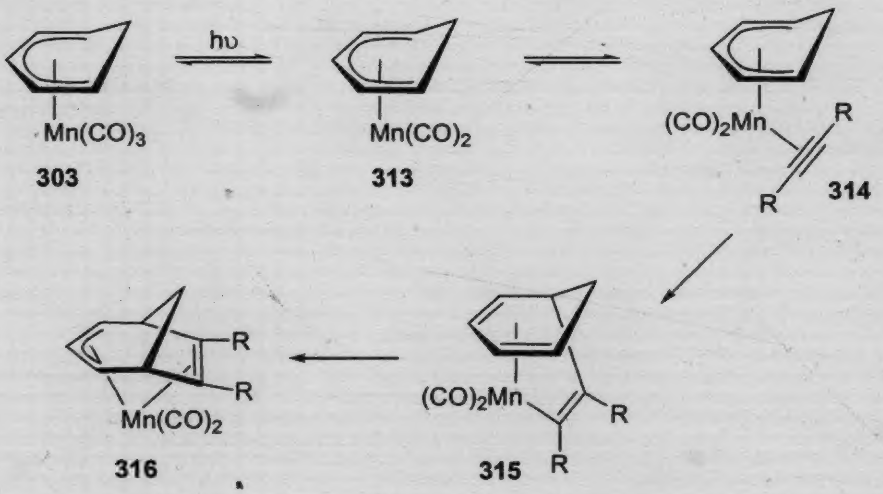
303: $R^1 = H$
307: $R^1 = Me$
308: $R^1 = Tol$

304: $R^1 = H$, $R^2 = R^3 = Me$, 90%
305: $R^1 = H$, $R^2 = R^3 = Ph$, 75%
309: $R^1 = H$, $R^2 = R^3 = Et$, 76%
310: $R^1 = H$, $R^2 = Me$, $R^3 = Ph$, 76%
311: $R^1 = Me$, $R^2 = R^3 = Ph$, 72%
312: $R^1 = Tol$, $R^2 = R^3 = Me$, 85%

Interestingly, Sheridan was able to employ an unsymmetrically substituted alkyne in a regioselective fashion; the single regioisomer obtained from this reaction was identified by X-ray crystallography.

Both Kreiter[186,187] and Sheridan[191-193] have offered similar proposals for the mechanism of photochemical seven-membered ring formation. The likely role of the ultraviolet irradiation is to open up a coordination site at the otherwise saturated metal center by ejection of a carbonyl ligand (Scheme **4.2**). The alkyne moiety then binds to the metal and subsequently inserts into a metal-carbon bond at one of the terminal pentadienyl carbons, forming the η^1,η^4-vinyl diene intermediate **315**. A second migratory insertion completes the annulation, forming the η^3,η^2-allyl olefin intermediate **316**. Although omitted for clarity from Scheme **4.2**, equilibria may exist between the unsaturated intermediates (**314**, **315**, and **316**) and their respective saturated tricarbonyl analogues.

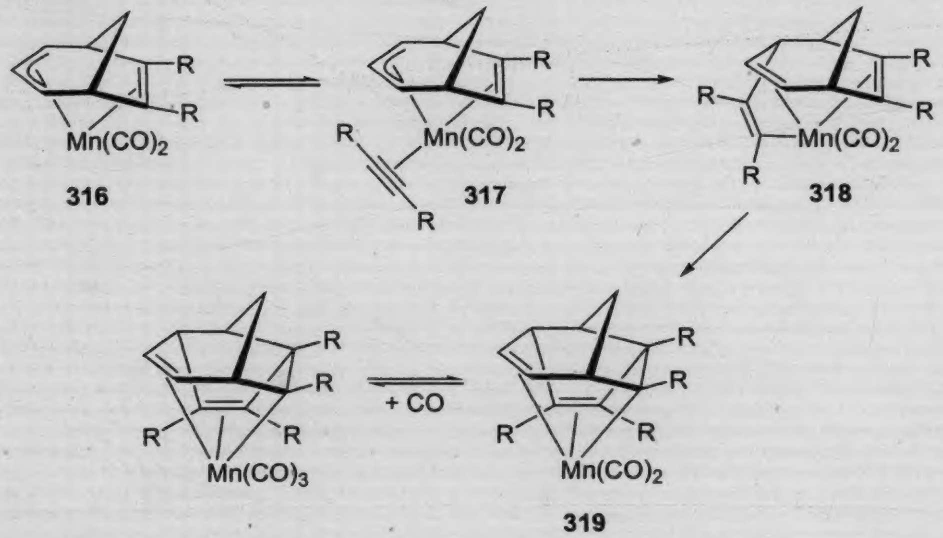
Scheme 4.2



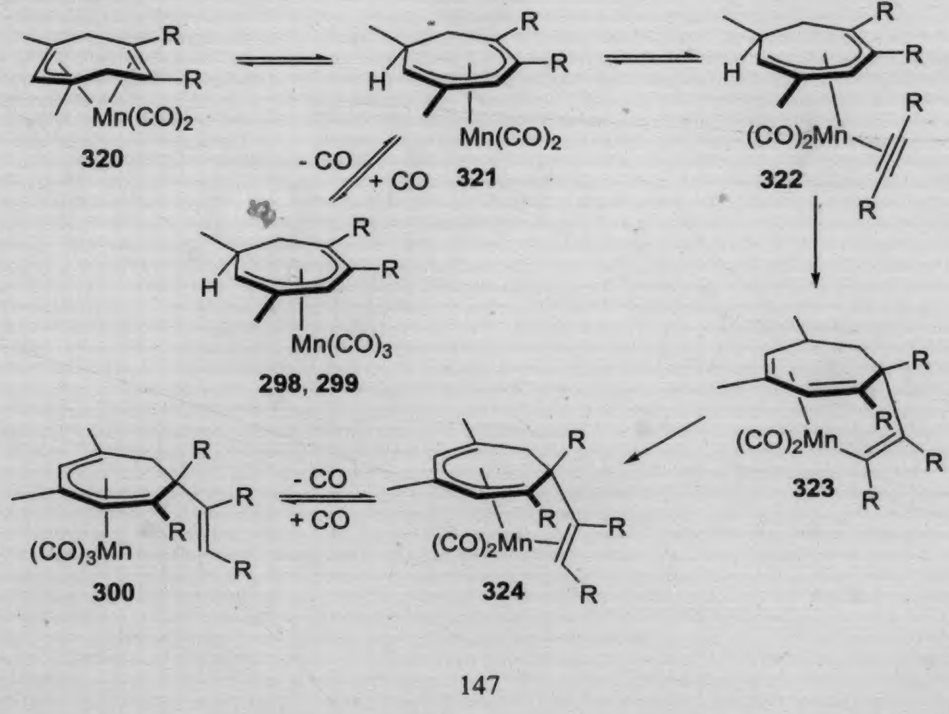
In those reactions employing closed pentadienyl complexes such as **301** or **303**, coordination of a second alkyne molecule and subsequent migratory insertion follow, affording the intermediate vinyl diene **318**. One final insertion reaction is required to generate the observed products (Scheme **4.3**).

In those reactions involving open pentadienyl substrates (Scheme **4.4**), the allyl olefin intermediate **320** (analogous to the bridged intermediate **316**) instead rapidly isomerizes to conjugated cycloheptadienyl complex **321** prior to any carbonyl or alkyne coordination; this isomerization is geometrically prohibited in bridged allyl olefins such as **316**. Re-coordination of the carbonyl ligand at this point affords the cycloheptadienyl

Scheme 4.3

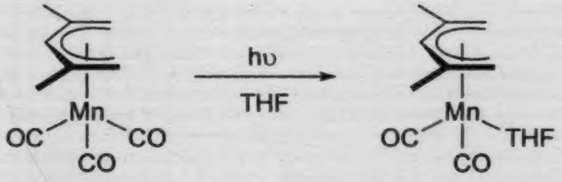

R
R
Mn(CO)2
316
R
R
R
Mn(CO)2
R
317
R
R
R
R
Mn(CO)2
R
318
R
R
R
R
Mn(CO)3
+ CO
R
R
R
R
Mn(CO)2
319

Scheme 4.4


R
R
Mn(CO)2
320
R
R
H
Mn(CO)2
321
- CO
+ CO
R
R
H
Mn(CO)3
298, 299
R
R
H
(CO)2Mn
R
R
322
R
R
(CO)2Mn
R
R
323
R
R
R
(CO)2Mn
R
324
- CO
+ CO
R
R
R
(CO)3Mn
R
300

manganese tricarbonyl products **298** and **299** isolated in some cases by Kreiter. Alternatively, coordination of a second alkyne followed by another insertion reaction leads to the alternate bis-adduct **300** that was obtained in other cases.

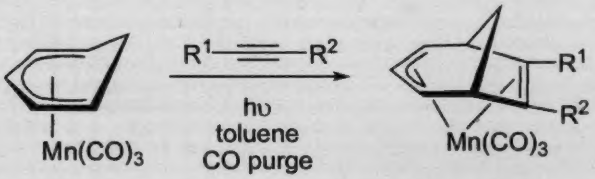
Kreiter and Sheridan both favor photo-induced carbonyl dissociation as the likely pathway by which a coordination site is created at the metal center. In some studies, Kreiter has prepared the solvent-stabilized dicarbonyl manganese complex **325** prior to thermal alkyne addition with no significant change in reaction yield (Equation **4.7**). Sheridan does, however, identify an alternative pathway in which the open coordination site is generated by a photochemically-induced slippage of the pentadienyl ligand to the η^3- mode; the subsequent reaction pathway is otherwise analogous to that proposed in Schemes **4.2**, **4.3** and **4.4**.



296 **325**

(Eq. 4.7)

The intermediacy of allyl olefin complexes has been supported by more recent efforts by Sheridan[193] to arrest the reaction after the initial [5+2] coupling. By limiting the amount of alkyne present and by conducting the reaction under a purge of CO gas in order to inhibit alkyne coordination to allyl olefin intermediates, [5+2] products **326** - **328** were isolated in low to moderate yields (Equation **4.8**). Double addition products were still the major species formed, but the arrested [5+2] adducts **326** - **328** were formed in significantly greater yield under the modified conditions, as compared to the standard photochemical conditions applied by Kreiter and Sheridan. The competency of allyl olefin products **326** - **328** toward further alkyne addition was also demonstrated; use of this protocol has also allowed for the formation of *mixed* alkyne bis-adducts.[193]



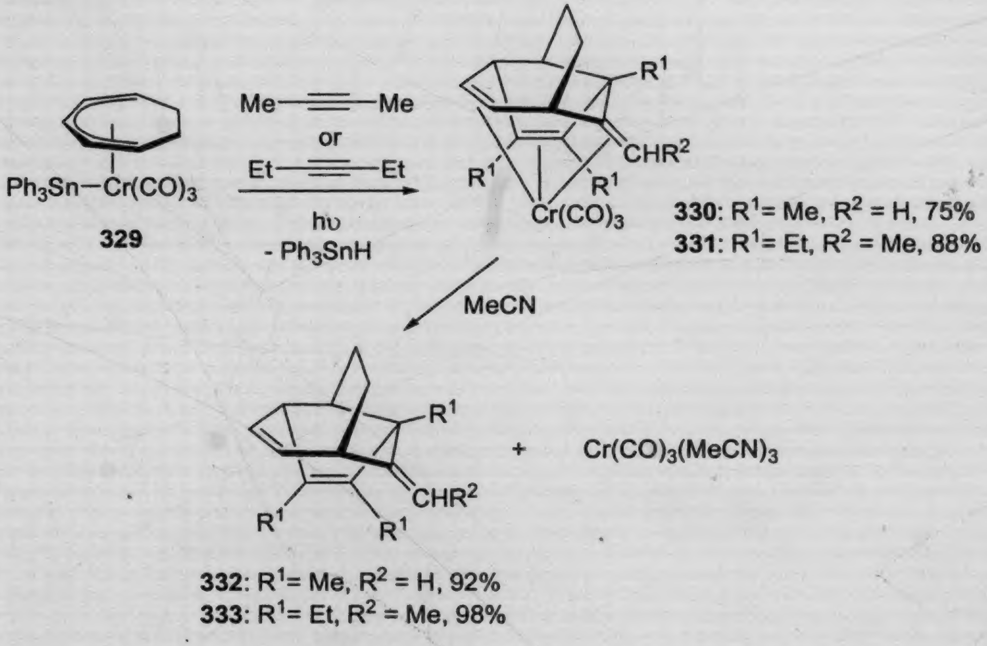
(Eq. 4.8)

303

326: R^1= H, R^2 = Ph, 16%
327: R^1= Me, R^2 = Ph, 21%
328: R^1 = R^2 = Ph, 39%

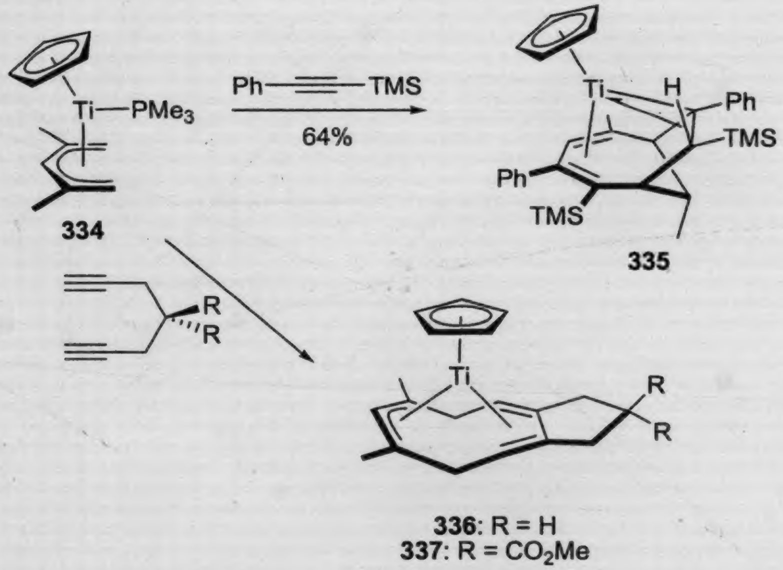
Sheridan has also reported the use of an interesting stannyl-chromium template for the mediation of the double alkyne addition reaction[192] (Scheme **4.5**). The reaction proceeds in a manner similar to that of the manganese-mediated process, except that the tricyclic Cr(II) product spontaneously reductively eliminates triphenyltin hydride to afford a Cr(0) species. The tricyclic ligand is readily decomplexed from the metal in good yield by simple dissolution in acetonitrile; the facile recovery of the organic product (**332** and **333**, for example) as well as the Cr(0) is an advantage of this protocol, although the generation of an equivalent of trialkyltin hydride is regrettable.

Scheme 4.5

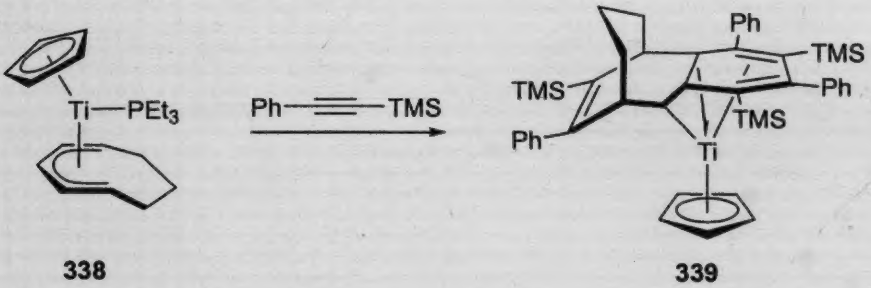

Ph3Sn—Cr(CO)3
329
Me—≡—Me
or
Et—≡—Et
hν
- Ph3SnH
R1
CHR2
R1
R1
Cr(CO)3
330: R1= Me, R2 = H, 75%
331: R1= Et, R2 = Me, 88%
MeCN
R1
CHR2
R1
R1
+
Cr(CO)3(MeCN)3
332: R1= Me, R2 = H, 92%
333: R1= Et, R2 = Me, 98%

Ernst has reported similar reactivity patterns in open and closed pentadienyl complexes of titanium[194-196] and zirconium.[196,197] The 16-electron half-open titanocene **334** reacts with two equivalents of phenyl trimethylsilylacetylene to furnish the bicyclic agostic complex **335** (Scheme **4.6**). Attempts to limit the alkyne incorporation to a single equivalent were unsuccessful, but heptadiynes were successfully incorporated to afford the nine-membered carbocyclic products **336** and **337**.

Scheme 4.6


Ti—PMe$_3$
Ph—≡—TMS
64%
334
Ti
H
Ph
TMS
Ph
TMS
335
R
R
Ti
R
R
336: R = H
337: R = CO$_2$Me

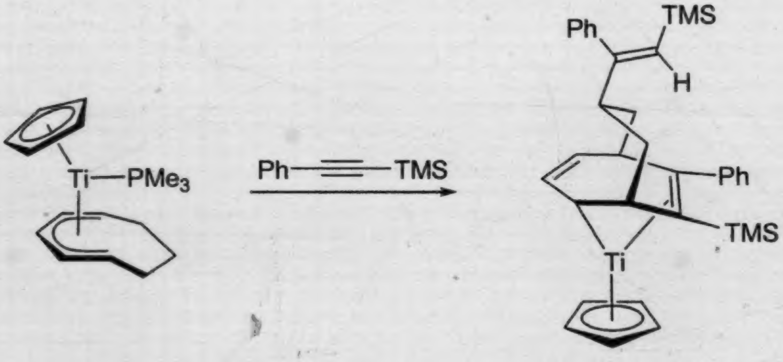
The analogous cyclooctadienyl complex **338** also incorporated phenyl trimethylsilylacetylene, although three equivalents of this alkyne were consumed, furnishing the tricyclic product **339** (Equation **4.9**).


Ti—PEt$_3$
Ph—≡—TMS
338
Ph
TMS
Ph
TMS
TMS
Ph
Ti
339

(Eq. 4.9)

Of particular interest to Ernst was the appearance of an unprecedented agostic interaction in **339** between at least one carbon-carbon bond and the metal; both of the mutually-bonded saturated carbons of the cyclohexadiene fragment lie in close proximity to the metal center, and the bond between these two carbons is unusually long.[196]

Interestingly, the closely related trimethylphosphine complex **340** incorporates only two equivalents of alkyne under the same conditions,[196] affording η^1-allyl-η^2-olefin complex **341** as the only product (Equation **4.10**).

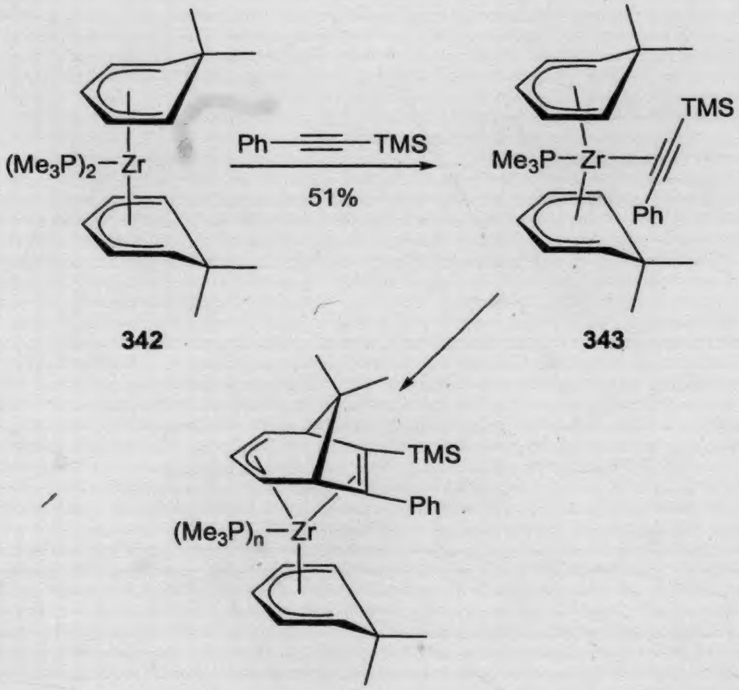


340 **341**

(Eq. 4.10)

Although no intermediates have been isolated from any of these titanium-mediated cycloadditions, a related reaction between the open zirconocene **342** and phenyl trimethylacetylene yields the alkyne complex **343** as an isolable intermediate (Scheme **4.7**). Upon standing in solution, complex **343** transforms into a single, as-yet unidentified product, which Ernst suggests might be the anticipated intermediate **344**, bearing either one or two coordinated phosphines.

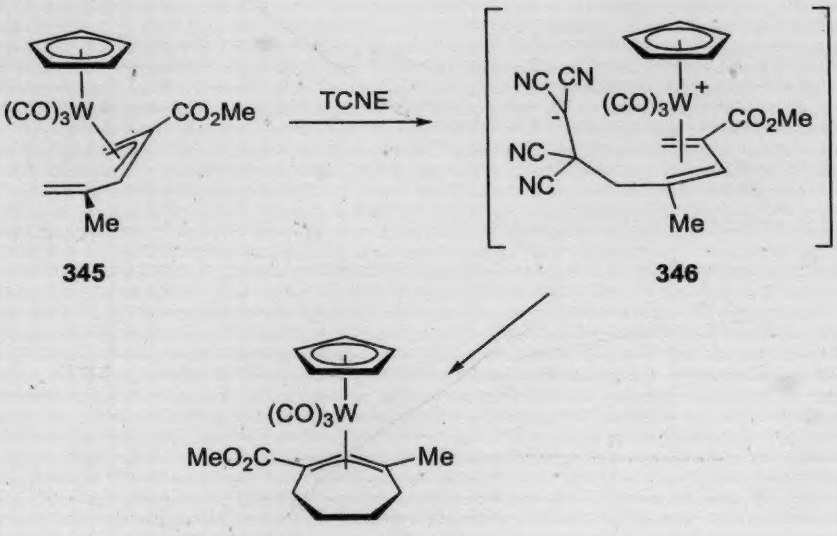
Scheme 4.7



342 **343** **344**

There exists only one report of a [5+2] cycloaddition of a pentadienyl ligand and an olefin. In 1996, Liu[198] described the interesting reaction of the tungsten η^3-pentadienyl complex **345** with tetracyanoethylene to produce the η^3-cycloheptenyl W(II) complex **347** in 64% yield under mild conditions (Scheme **4.8**). The reaction is very limited in scope; only TCNE is a competent olefin for the cycloaddition, prompting Liu to speculate that the mechanism may proceed via the zwitterionic intermediate **346**. In this proposal, the starting pentadienyl is bound in an η^3-fashion, and the initial carbon-carbon bond is formed at a non-coordinated olefinic terminus which is rendered nucleophilic by the electron-rich organotungsten substituent.

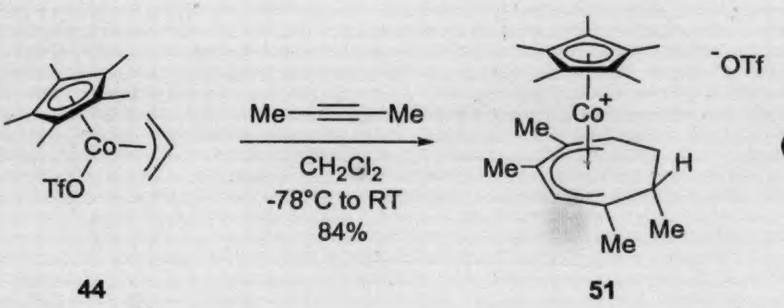
Scheme 4.8


(CO)$_3$W
CO$_2$Me
Me
345
TCNE
NC CN
NC
NC
(CO)$_3$W$^+$
CO$_2$Me
Me
346
(CO)$_3$W
MeO$_2$C
Me

347, 64%

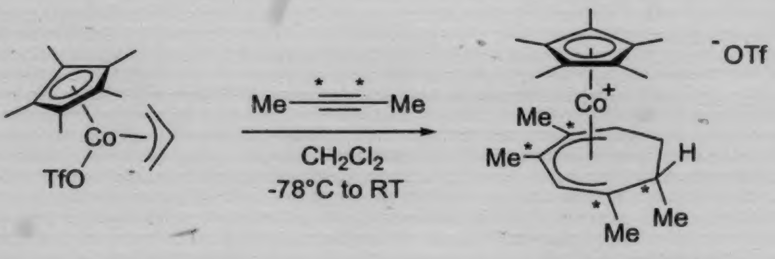
Part B: Cobalt(III) Pentadienyl Complexes as a Possible Intermediate in a [5+2] Ring-Expansion Process Involving a Carbon-Carbon Bond Activation

As part of the investigation and development of the Co(III)-mediated [3+2+2] allyl/alkyne cycloaddition in the Stryker group, as described in Chapter 2 of this document, Etkin observed[101] an unusual reaction in which treatment of the Cp*Co(III) allyl triflate **44** with 2-butyne yielded a Cp*Co(III) cycloheptadienyl complex **51** in which the three unsubstituted cycloheptadienyl carbons were *not* contiguous (Equation **4.11**). The formation of this anomalous cycloadduct **51** could only be rationalized by invoking a carbon-carbon bond activation pathway; either the allyl moiety is fragmented at some point during the course of the reaction, or some of the substituent methyl groups migrate about the carbon framework during the carbocyclization process.



(Eq 4.11)

Dzwiniel shed further light on this novel C-C bond activation chemistry,[17,101,103] demonstrating via ^{13}C-labeling experiments (Equation **4.12**) that the 2-butyne fragments remain intact in the product cycloheptadienyl fragment, indicating that the carbon-carbon bond activation must involve two of the carbons originating in the allyl moiety of the starting Co(III) complex **44**.



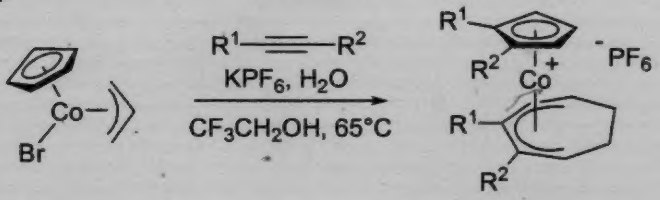
Co
TfO
Me—≡—Me
CH2Cl2
-78°C to RT
Co+
-OTf
Me
Me
H
Me
Me

(Eq 4.12)

44

51b

Dzwiniel further explored this “anomalous” [3+2+2] chemistry, extending the studies to include templates based on cyclopentadienyl ligands other than the ubiquitous Cp* ligand.[101] In some cases, the carbon-carbon bond activation pathway leads to an astonishing rearrangement in which the cyclopentadienyl moiety is not chemically innocent at all, but is instead expanded by two carbons into a new 7-membered cycloheptadienyl ligand (Equation **4.13**).



Co
Br
R1—≡—R2
KPF6, H2O
CF3CH2OH, 65°C
R1
R2
Co+
-PF6
R1
R2

(Eq. 4.13)

348

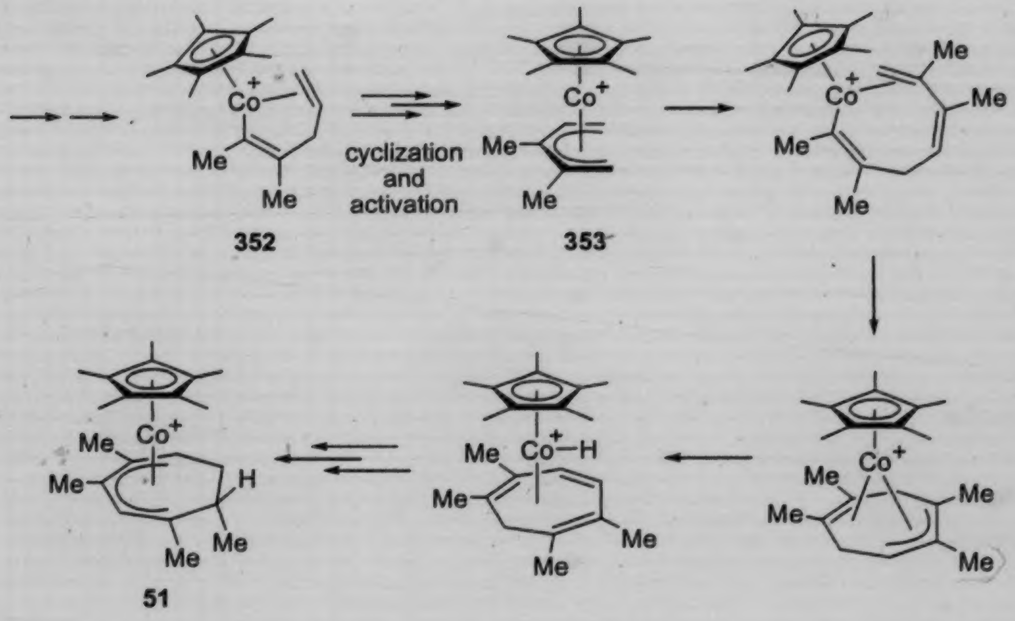
349: R^1 = *t*-Bu, R^2 = H
350: R^1 = *t*-Bu, R^2 = Me
351: R^1 = Ph, R^2 = Me

The mechanistic rationalization for the observed carbon-carbon activation and alkyne incorporation chemistry remains a thought-provoking problem, as many of the reactive intermediates that have been proposed by Dzwiniel (and, more recently, by others) cannot be isolated or trapped for testing of competency. Nonetheless, there are several reasonable mechanistic possibilities that all involve rearrangements that occur after the formation of a vinyl-olefin intermediate (such as **352**, Scheme **4.9**) from the initial insertion of the first alkyne moiety into the allyl-metal bond. Each of the following proposals may be viewed as a divergence from the "normal" [3+2+2] pathway at this point; an overview of the proposed [3+2+2] pathway is presented in Chapter 2 of this thesis (Scheme **2.11**).

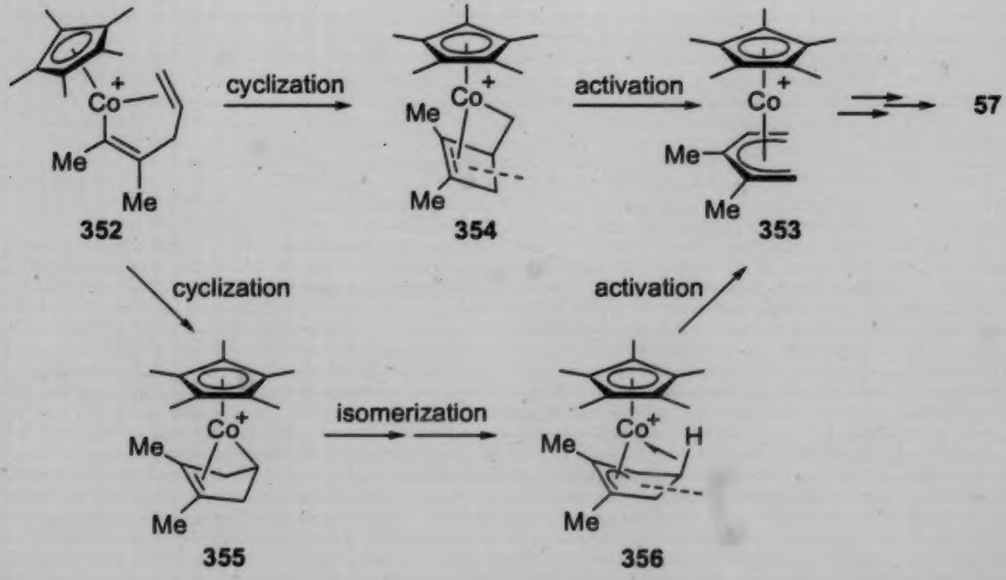
Dzwiniel identified one such possibility (Scheme **4.9**), which implicates the formation of a Co(III) η^5-pentadienyl complex **353** as a potentially isolable intermediate on the reaction pathway. Dzwiniel proposed that such an intermediate might proceed to the observed cycloheptadienyl product **51** upon coordination and insertion of an additional alkyne unit, followed first by a migratory cyclization event and then by a metal-mediated conjugation of the unsaturated carbon atoms through a sequence of β-hyride elimination and migratory insertion reactions (Chapter 2, Part A).

The formation of the requisite open pentadienyl complex **353** could, in principle, arise from the proposed vinyl olefin intermediate **352** via a migratory cyclization to generate either a four-membered or a five-membered ring (Scheme **4.10**); vinyl olefin complexes such as **352** are proposed as early intermediates along the "normal" [3+2+2]

Scheme 4.9


cyclization
and
activation
Co+
Me
352
353
51

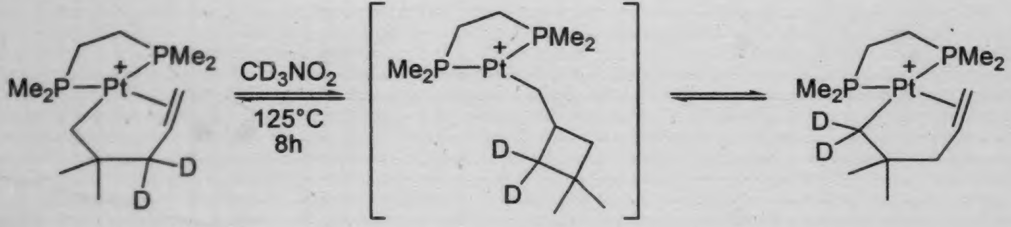
Scheme 4.10


cyclization
activation
cyclization
activation
isomerization
Co+
Me
H
352
354
353
57
355
356

pathway. In the former case, the vinyl olefin **352** does not coordinate a second alkyne unit as required for a "normal" [3+2+2] reaction, but instead undergoes a migratory ring-closure to generate the cationic 16-electron (cyclobutenyl)methyl complex **354**. Activation of the carbons β and γ to the metal in intermediate **354**, perhaps by an electrocyclic ring-opening, thus affords the postulated pentadienyl complex **353**.

Flood[199] has observed a similar reversible four-membered ring closure and activation in a Pt(II) system (Scheme **4.11**) and has estimated a ring strain energy of approximately 28 kcal/mol for the cyclobutane ring; the release of a similarly high ring-strain energy would likely be the driving force for a postulated carbon-carbon activation of complex **354**.

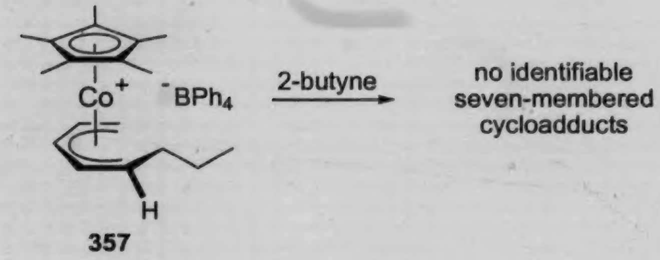
Scheme 4.11



It must be borne in mind, however, that this large ring-strain energy might also act to impede the kinetic formation of 4-membered ring complex **354** in favor of the less-strained 5-membered alternative **355** (Scheme **4.10**). Were the η^3-agostic allyl complex **356** to form from **355** via β-hydride elimination and reinsertion, the subsequent carbon-carbon bond activation would alleviate less ring strain than in the corresponding 4-membered ring alternative. Nonetheless, cyclizations forming cyclopentenyl complexes clearly derived from **355** are known and agostic allyl complexes related to **356** are known to proceed on to give η^5-cyclopentadienyl complexes after formal loss of dihydrogen.

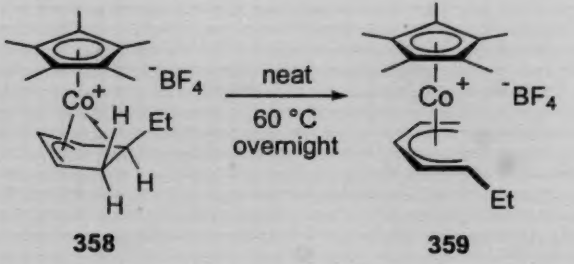
For η^5-pentadienyl complex **353** to be a competent intermediate in the formation of cycloheptadienyl complexes, it must react to incorporate a second equivalent of alkyne and then close to a seven-membered ring under mild conditions; this must be the case regardless of the pathway by which **353** is obtained. Since this pentadienyl complex is formally an 18 electron species when the pentadienyl ligand is bound in the η^5-mode, it is likely that the pentadienyl ligand would need to at least temporarily access an η^3-binding mode in order to permit coordination and insertion of a second alkyne.

Dzwiniel[17] tested the competency of one Cp*Co(III) pentadienyl complex for intermediacy in seven-membered ring formation. The cationic (η^5-C_5Me_5)Co(III) (η^5-1-*anti*-propylpentadienyl) tetrafluoroborate complex **357** was prepared in accordance with the literature[200] and subsequently treated with 2-butyne. The reaction was attempted at room temperature as well as at 60 °C, but in neither case was a recognizable seven-membered ring complex detected in the product mixture (Equation **4.14**). No other pentadienyl complex was investigated by Dzwiniel and it is noteworthy that complex **357** is an atypical representative of the family of η^5-pentadienyl complexes: the 1-propyl substituent in **357** is in the *anti*-configuration and *endo* to the metal, whereas the vast majority of terminally substituted pentadienyl complex bear the substituent in a *syn*-configuration, *exo* to the metal.


Co+
-BPh4
H
357
2-butyne
no identifiable seven-membered cycloadducts

(Eq. 4.14)

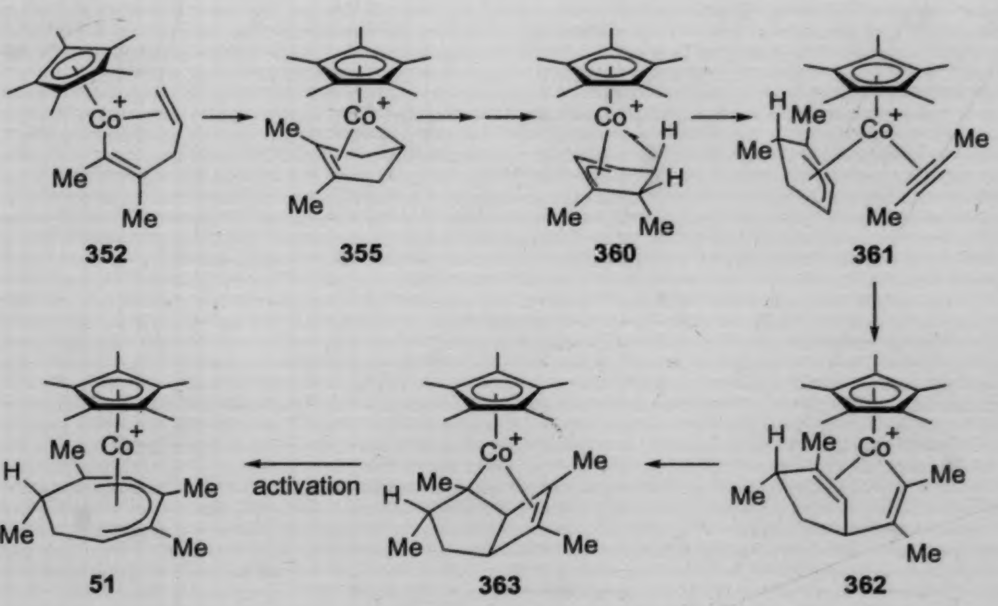
Spencer[172,200,201] has prepared several complexes structurally similar to the proposed agostic allyl intermediate **356**. The ethyl-substituted analogue **358**, well-studied and characterized, is known to resist carbon-carbon bond activation unless heated to elevated temperatures under strictly anhydrous conditions (Equation **4.15**). Since the anomalous [3+2+2] cycloadducts are, in fact, formed at temperatures ranging from -78 ˚C to room temperature, it is thus highly unlikely that an allyl-agostic intermediate such as **356** could lie on the reaction pathway for the formation of **51**.


Co+
-BF4
H
Et
H
H
358
neat
60 °C
overnight
Co+
-BF4
Et
359

(Eq. 4.15)

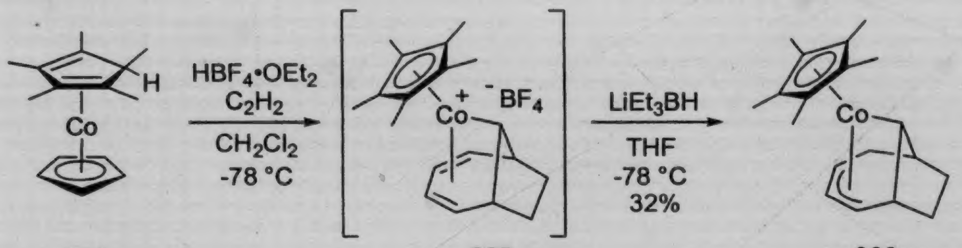
A second carbon-carbon bond activation pathway was also proposed by Dzwiniel[17] that is not dependant on the intermediacy of a cationic open pentadienyl complex of Co(III), but is still requires the formation of an agostic allyl complex (Scheme **4.12**). In this alternative mechanism the allyl-agostic species **360**, which is isomeric to **356**, proceeds to an 18-electron allyl alkyne intermediate **361** upon replacement of the agostic interaction with the coordination of a second alkyne. Migratory insertion of this alkyne into the allyl-metal bond leads to vinyl olefin complex **362** which could, in turn, generate the [3.2.0] bicyclic ring intermediate **363** upon further migratory insertion. Subsequent activation of the strained cyclobutene bond in **363**, an allowed disrotatory cycloreversion in the presence of metal-coordination,[202,203] would thus furnish the observed cycloheptadienyl product **51** directly; no subsequent carbon-hydrogen activation or re-insertion steps are necessary in this pathway.

Scheme 4.12


Co+
Me
Me
352
Co+
Me
Me
355
Co+
H
H
Me
Me
360
H
Me
Me
Co+
Me
Me
361
Me
Co+
H
Me
Me
Me
51
activation
Co+
Me
H
Me
Me
Me
Me
363
H
Me
Co+
Me
Me
Me
362

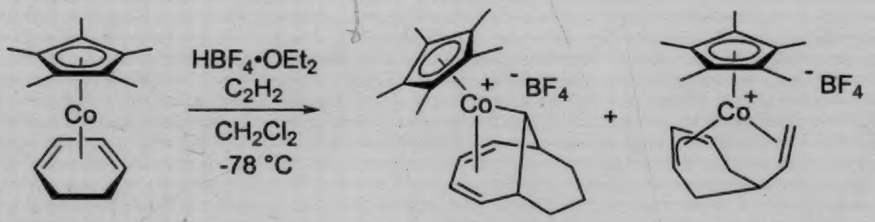
Prior to Dzwiniel producing his dissertation, there was no direct evidence for the ability of agostic allyl complexes to react by migratory insertion with alkynes, as required by this mechanism (Scheme **4.12**). Dzwiniel did, however, isolate an apparent product of such an insertion from the agostic allyl complex formed upon protonation of **364** in the presence of acetylene (Scheme **4.13**).[17]

Scheme 4.13


H
Co
$HBF_4 \cdot OEt_2$
C_2H_2
CH_2Cl_2
-78 °C
+
- BF_4
Co
$LiEt_3BH$
THF
-78 °C
32%
Co

364 **365** **366**

Subsequently, Older[102,104,204,205] in the Stryker group also demonstrated this same insertion process in some agostic allyl complexes of ruthenium. Even more recently, Chan[206] in the Stryker group demonstrated that the 6-membered agostic allyl complex formed upon protonation of **105** will incorporate either one or two alkyne fragments, affording the bis-adduct **106** or the mono-adduct **107** respectively (Equation **4.16**).

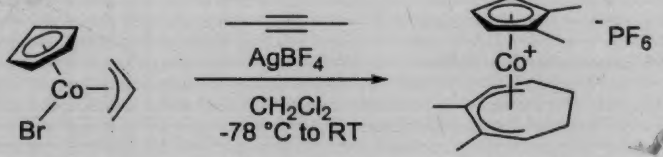

Co
$HBF_4 \cdot OEt_2$
C_2H_2
CH_2Cl_2
-78 °C
+
- BF_4
Co
+
+
- BF_4
Co

(Eq 4.16)

105 **106** **107**

Although Chan has thus demonstrated that cyclic agostic allyl complexes may participate in migratory insertion reactions with alkynes, it is noteworthy that there remains no evidence for the formation of an eight-carbon [4.2.0] ring system (homologous to **363**) in Chan's chemistry, nor for any subsequent C-C bond activation of any such system.

One compelling feature of a mechanism proceeding via agostic allyl complexes (Scheme **4.12**) is that such a mechanism could also readily account for the formation of all "anomalous" [3+2+2] cycloadducts in which cyclopentadienyl ligands are activated and modified (Equation **4.13**). In the case of CpCo(III) allyl bromide **348**, reaction with excess 2-butyne in the presence of silver tetrafluoroborate affords, albeit in very low yield, the rearranged product **367** (Equation **4.17**).



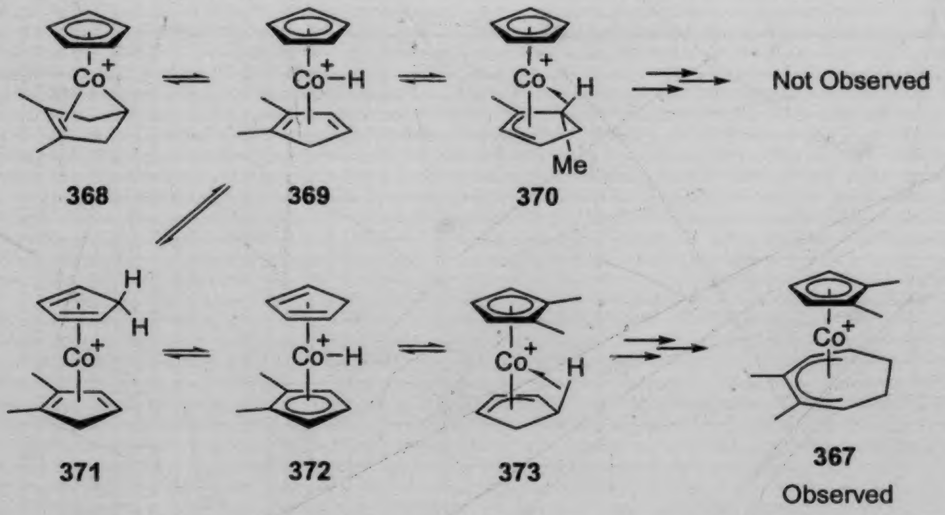
348 **367**

(Eq. 4.17)

Stryker has proposed that such a rearrangement is consistent with the intermediacy of agostic η^3-cyclopentenyl complexes. Upon formation of σ,π-intermediate **368** by cyclization of the corresponding vinyl olefin complex, a pair of isomeric allyl olefin complexes, **370** and **373**, are accessible (Scheme **4.14**). It is likely that **370** and **373** rapidly interconvert via a stepwise metal-mediated hydride-transfer sequence as shown, although only the product arising from **373** is ultimately obtained, presumably by alkyne coordination and carbon-carbon bond activation (Scheme **4.12**).

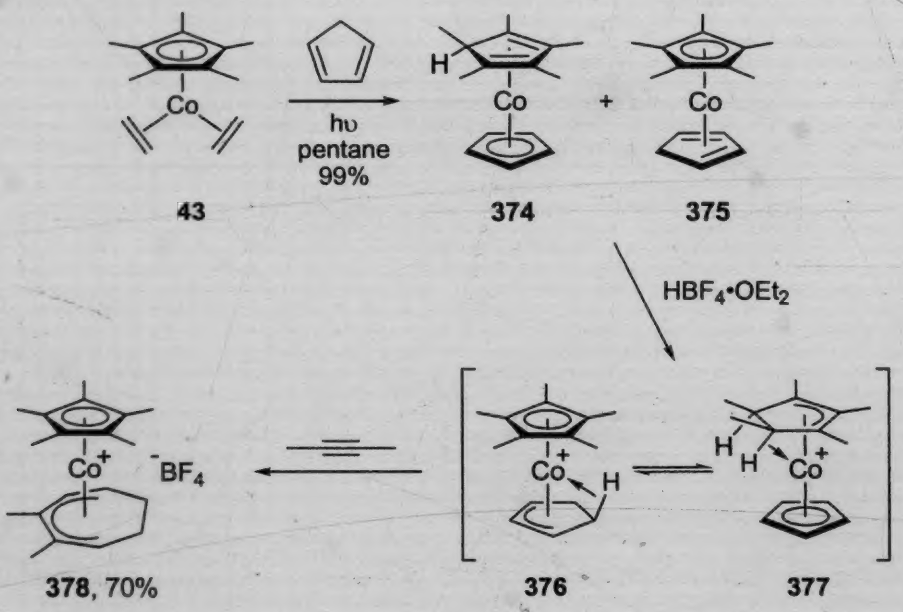
An interesting implication of this proposed mechanism is the intermediacy of cationic cyclopentadienyl cyclopentadiene hydride Co(III) complexes **369** and **372**. If such species are competent intermediates in anomalous [3+2+2] reactions of this type, it

Scheme 4.14



might be possible to also generate these intermediates by protonation of stable Co(I) η^4-cyclopentadiene complexes and, by doing so in the presence of an alkyne, observe an entirely unprecedented [5+2] cycloexpansion process. Dzwiniel pursued this strategy and successfully demonstrated a number of [5+2] ring expansion reactions of various Co(I) cyclopentadiene complexes and alkynes.[17,103] In one representative example (Scheme **4.15**), protonation of a mixture of Co(I) complexes **374** and **375** in the presence of excess 2-butyne afforded **378** as the only seven-membered ring product; a small amount of $[Cp^*CoCp]^+ BF_4^-$ was also formed. Starting complexes **374** and **375** were prepared as a mixture by ultraviolet irradiation of the bis(ethylene) complex **43** in the presence of cyclopentadiene. The composition of this mixture varied from run to run, depending on the irradiation time, and the tautomeric products could not be separated and do not

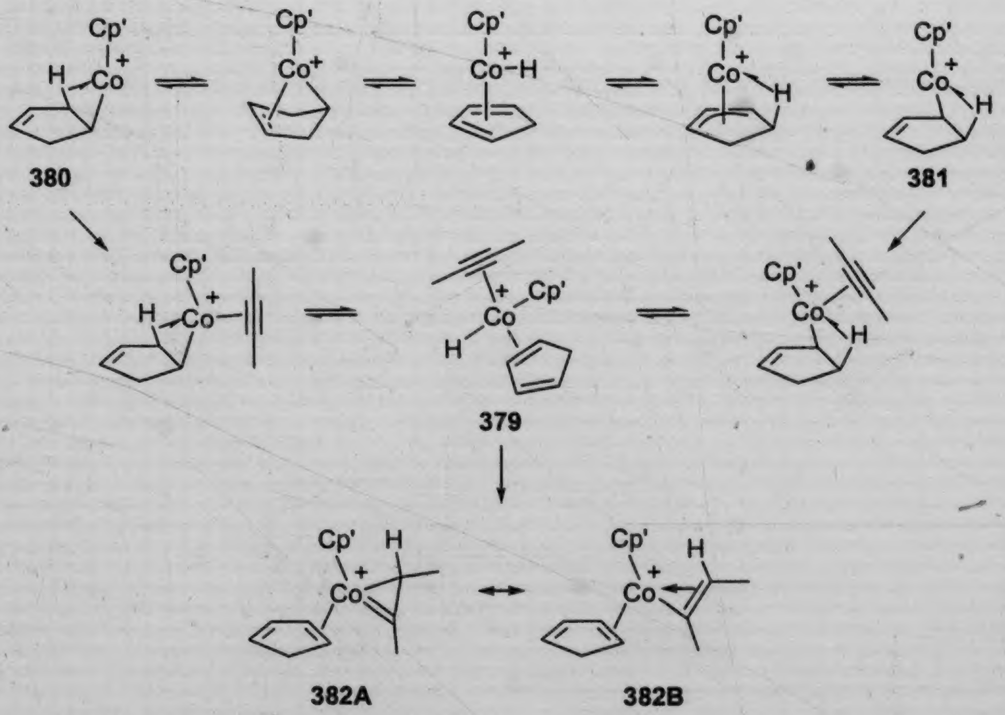
Scheme 4.15



equilibrate thermally. Regardless of the actual ratio of **374** to **375**, the isolation of a single cycloheptadienyl complex suggests that, upon protonation, **374** and **375** respectively furnish rapidly equilibrating cationic agostic complexes **376** and **377**; of these complexes, only **376** reacts further with alkyne to eventually yield **378**.

Dzwiniel not only unearthed this interesting and potentially useful new [5+2] ring expansion, but also added support to the proposed mechanism (Scheme **4.14**) for the formation of anomalous [3+2+2] products. More recent preliminary theoretical work by Ammal and Nakamura in collaboration with the Stryker group[207] has revealed a third possible mechanism which, at least computationally, is the only pathway not involving an energetic discontinuity in the computed mechanism (Scheme **4.16**). As with the previous proposal, this mechanism invokes the intermediacy of a cationic Co(III) hydride (e.g. **369** or **372**) in rapid equilibrium with η^3-cyclopentenyl agostic complexes akin to **376**; it is in the subsequent bond-forming event that the calculations diverge from the pathway described in Scheme **4.12**.

Scheme 4.16

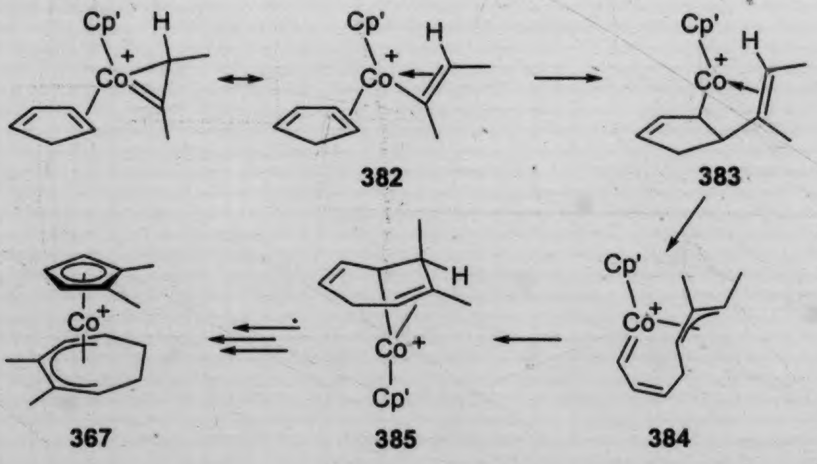


Instead of proceeding from an agostic allyl intermediate such as **360** to a vinyl olefin complex such as **362** (Scheme **4.12**), the calculations suggest the formation of the

18-electron η^2-cyclopentadiene alkyne hydride complex **379**, formed either from the σ-agostic intermediate **380** or from the η^1-agostic allyl complex **381**. The interesting intermediate **382**, which may be described either as a cobaltacyclopropene (**382A**) or as an η^2-vinyl complex (**382B**), is formed upon insertion of the alkyne into the metal-hydride bond of **379**.

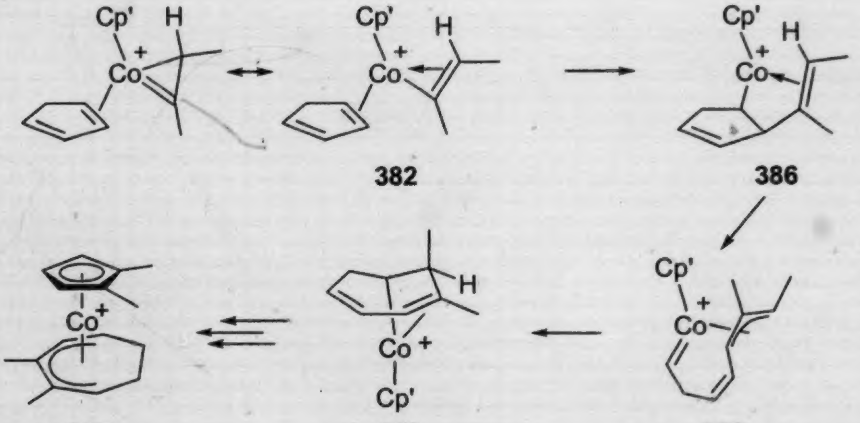
There are two very similar possibilities for the further transformation of intermediate **382** into the cycloheptadienyl product, depending on the regioselectivity of the migratory insertion of the η^2-cyclopentadiene ligand into the cobalt-vinyl bond. One such insertion regiochemistry (Scheme **4.17**) results in an η^1-allyl olefin intermediate **383**, which is then poised to activate the C_α-C_β bond to afford the allyl carbene **384**.

Scheme 4.17



If the migratory insertion from **382** proceeds with the alternative regiochemistry (Scheme **4.18**), the σ,π-intermediate **386** is generated, which then activates the β-C-C bond to afford the allyl carbene complex **387**. In either case, the allyl carbene complex can form a seven-membered ring via a formal reductive elimination to form either **385** or **388** respectively; the observed product **367** is ultimately realized through metal-mediated β-hydrogen isomerization.

Scheme 4.18



382

386

367

388

387

Although the computational studies have identified what appears to be the pathway for the formation of "anomalous" [3+2+2] cycloadducts via carbon-carbon activation, the possibility that Co(III) η^5-pentadienyl complexes might also incorporate alkynes to form seven-membered rings cannot be ruled out; as described previously, Dzwiniel only briefly examined the reactivity of a single (and atypical) Co(III) η^5-pentadienyl species. Even if such complexes do not lie along the "anomalous" [3+2+2] energy surface, the work of Kreiter, Sheridan, and Ernst described in Part A of this chapter suggests that the potential exists for a thermal or photochemical [5+2] cycloaddition process which is complementary to the existing [3+2+2] methodology. In those few cases in which Sheridan[193] was able to isolate a simple [5+2] monoadduct

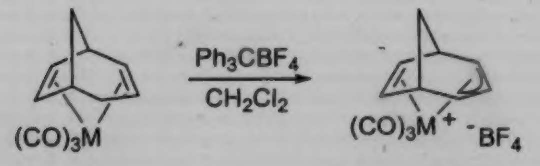
(Equation **4.8**), the product exhibited an interesting non-conjugated *bridged* η^3,η^2-allyl olefin ligand. If a related cycloaddition were to proceed on an *acyclic* Co(III) template, the analogous Co(III) η^3,η^2-cycloheptadienyl product would represent an unprecedented and potentially valuable alternative to the η^5-cycloheptadienyl products typical of Co(III)-mediated [3+2+2] cycloadditions.

Part C: 1,2,4,5,6-η^2,η^3-Cycloheptadienyl Complexes in Organometallic Chemistry

Although the isolated products arising from [3+2+2] cycloadditions of acyclic allyl ligands contain fully conjugated η^5-cycloheptadienyl ligands, other binding modes are potentially available for this cyclic ligand. The η^1,η^4-cycloheptadienyl coordination mode is proposed as an intermediate in the [3+2+2] cycloadditions process; ^{2}H-labelling studies performed by Dzwiniel and Etkin strongly support the intermediacy of such "σ-alkyl/diene" species that are not isolable or observable under the normal [3+2+2] reaction conditions, but which are obtained from reaction of *cyclic* allyl intermediates (e.g. Equation **4.16**). The η^1,η^4-coordination mode for simple *unbridged* cycloheptadienyl complexes is precedented only by those Ru(II) systems described by Older.[102,104,204,205]

The other possible nonconjugated bidentate η^5-binding configuration for the cycloheptadienyl ligand is the η^3,η^2-coordination mode, in which the coordinated carbon fragments bind as isolated allyl and olefin fragments. Among eight-membered rings, this binding mode has been reported for a number of bridged and unbridged transition metal complexes, including those of Ru,[208-220] Rh,[221-228] Ir,[227-232] Co,[113,228,233] Mo,[234-236] W,[237] and Ti.[194] A few nine-membered examples have also been reported by Kreiter[182,183,185] and Ernst.[238]

Despite the number of large-ring carbocyclic ligands exhibiting the η^3,η^2-binding motif, only a few examples have been reported for the cycloheptadienyl series, all of which contain a bridge to prohibit isomerization to the fully conjugated η^5-coordination mode. The first example of such a bridged bicyclic cycloheptadienyl was reported by Rosenblum in 1965.[239] The cationic Fe(II) carbonyl complex **390** was prepared in undisclosed yield by the reaction of bis(alkene) complex **389** with trityl hexafluorophosphate (Equation **4.18**); X-ray crystallography confirmed the bicyclic η^3,η^2-structure. The related chemistry of ruthenium analogues was demonstrated several years later by Lewis and colleagues.[240]

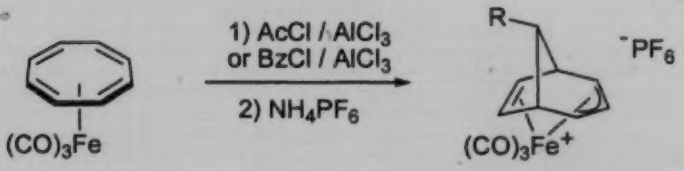


389 (M = Fe)
391 (M = Ru)

390 (M = Fe)
392 (M = Ru, 53%)

(Eq. 4.18)

Analogous Fe(II) complexes **394** and **395** were also prepared[241-244] by a novel rearrangement of the precursor COT complex **393** (Equation **4.19**). The cationic carbonyl products were further converted to the neutral iodides in a subsequent nucleophilic addition. Polborn[245] has since used complexes of this type to make some interesting heterobimetallic complexes with rhenium.



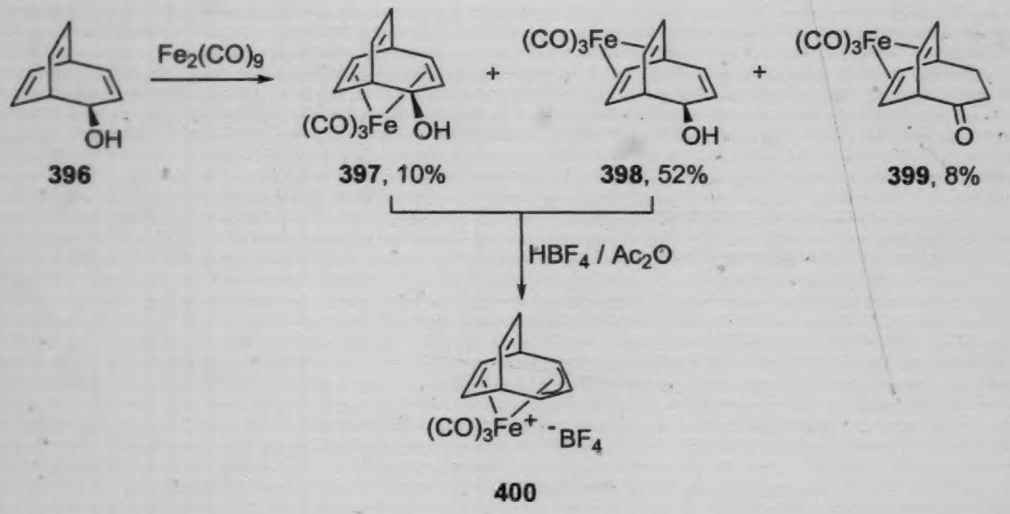
393

394 (R = Ac, 47%)
395 (R = Bz, 74%)

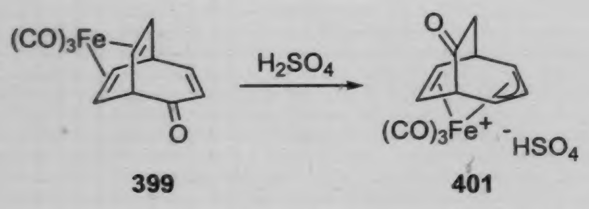
(Eq. 4.19)

The first example of a 2-carbon bridged η^3,η^2-complex was described by Eisenstadt in 1970.[246] In this early work, iron complex **400** bearing a bicyclo[3.2.2]nonadienyl ligand was prepared by protonation of the iron(0) diene complexes **397** and **398**, although no yields were reported for the formation of **400** from either precursor.

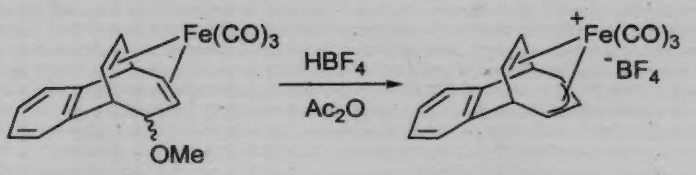
Scheme 4.19


Fe2(CO)9
396
(CO)3Fe
OH
397, 10%
+
(CO)3Fe
OH
398, 52%
+
(CO)3Fe
O
399, 8%
HBF4 / Ac2O
(CO)3Fe+ -BF4
400

Additionally, Eisenstadt prepared **401** from protonation[246] of the Fe(0) complex **399** (Equation **4.20**) and the analogous benzo species **404** from **403** in a related fashion (Equation **4.21**).[247]


(CO)3Fe
O
399
H2SO4
O
(CO)3Fe+ -HSO4
401

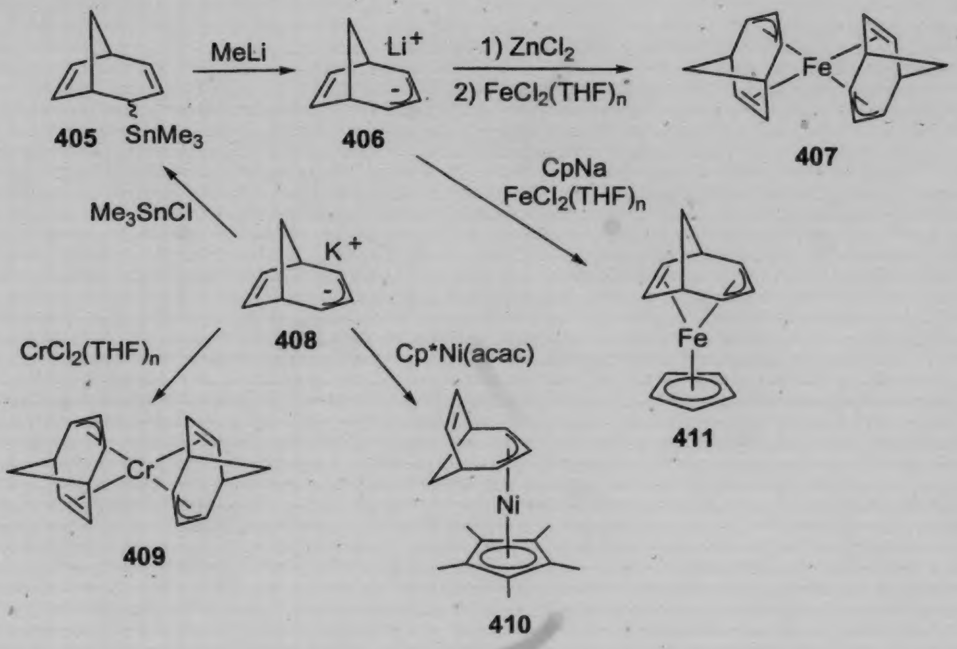
(Eq. 4.20)


Fe(CO)3
HBF4
Ac2O
+Fe(CO)3
-BF4
OMe

403 **404** **(Eq. 4.21)**

More recently, Köhler and coworkers have described[248] the preparation of several complexes bearing one-carbon-bridged η^3,η^2-cycloheptadienyl ligands (Scheme **4.20**). Unlike previous investigators, Köhler introduces the intact hydrocarbon ligand as a nucleophile. The eight-carbon bicyclo[3.2.1]octa-2,6-dien-4-yl anion was added to transition metal salts to generate various complexes of iron (**407** and **411**), chromium (**409**), and nickel (**410**). In the latter case, the bicyclic ligand binds only as an η^3-allyl

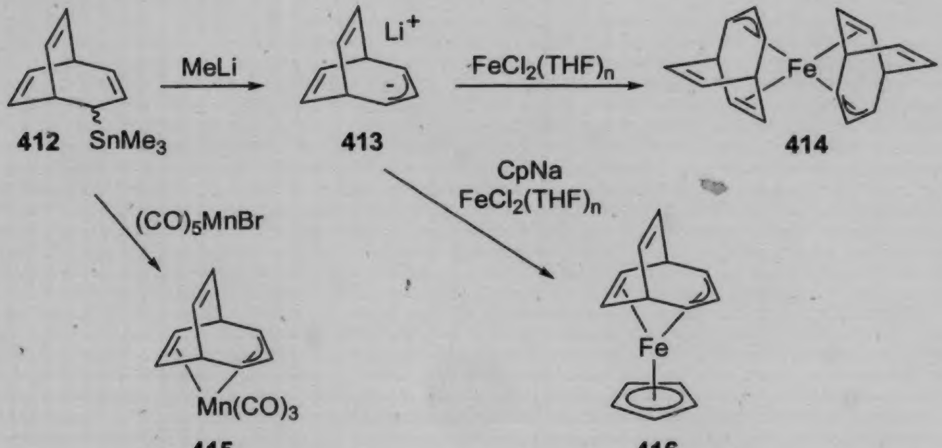
Scheme 4.20


405
SnMe3
MeLi
Li+
406
1) ZnCl2
2) FeCl2(THF)n
Fe
407
Me3SnCl
K+
408
CpNa
FeCl2(THF)n
CrCl2(THF)n
Cp*Ni(acac)
Cr
409
Ni
410
Fe
411

moiety as this is sufficient to achieve an 18-electron count at the metal. Interestingly, the Cp*Ni fragment of complex **410** is situated on the *exo* face of the bicyclooctadienyl ligand, as shown.

Along similar lines, several complexes bearing the 9-carbon bicyclo[3.2.2]-nona-2,6,8-trien-4-yl (BCNT) ligand were also synthesized by Köhler[248] (Scheme **4.21**).

Scheme 4.21

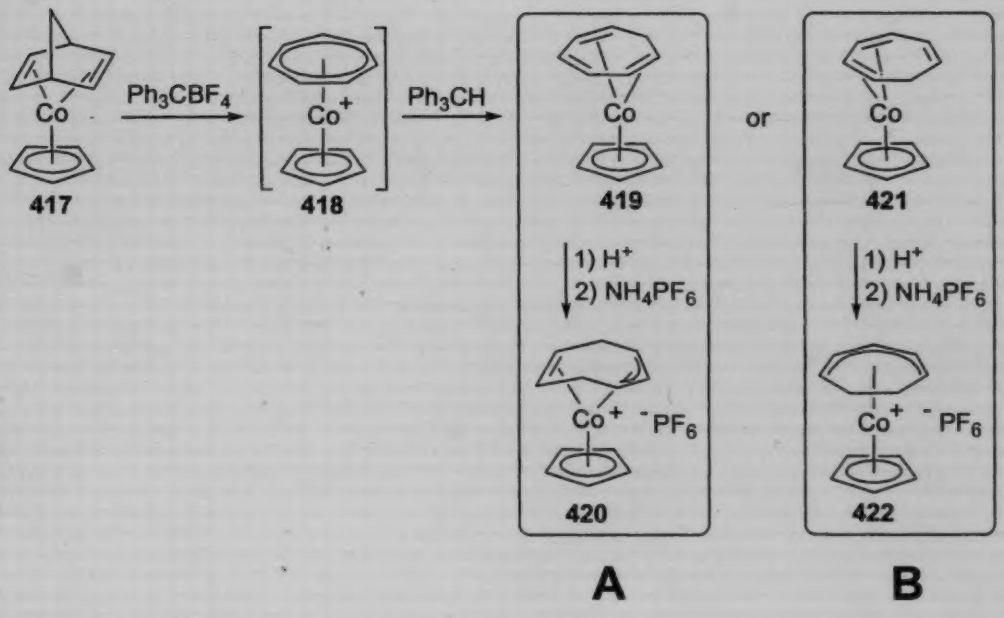


412 **413** **414** **415** **416**

Only one account exists of a simple monocyclic η^3,η^2-cycloheptadienyl ligand, although the complex was, in all likelihood, misidentified. In 1969, Lewis[249] reported the unexpected formation of a cyclohepta-2,5-dienyl complex of Co(III) upon treatment of CpCo(I) norbornadiene **417** with trityl tetrafluoroborate and subsequent aqueous work-up. Lewis described the product of the reaction, isolated as the water-insoluble hexafluorophosphate salt, as an orange-red salt, which decomposes slowly in acetone solution. Apart from an elemental analysis, almost no characterization data was reported by Lewis, other than the existence of a signal at 5.6 ppm in the ^{1}H NMR spectrum which corresponded to the cyclopentadienyl ligand. Lewis did, however, report the presence of nine or ten additional proton resonances in the spectrum and only speculated that the ultimate product from the reaction is the cationic complex **420**.

Lewis also proposed a pathway for the ultimate formation of **420**. Winstein had previously shown[250] that the 7-norbornadienyl cation rearranges to the tropylium ion in solution; Lewis suggested a similar rearrangement might be possible for the cobalt-bound ligand to afford a cationic tropylium complex **418**. Dauben had previously reported[251] the inability of trityl cation to abstract hydride from the *neutral* cycloheptatriene Fe(0) carbonyl complex, but Lewis proposed that a *cationic* CpCo(III) tropylium complex **418**, if formed, might be sufficiently electrophillic so as to abstract a hydride back from the

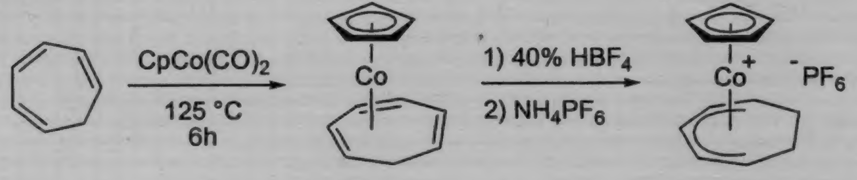
Scheme 4.22



triphenylmethane, regenerating the trityl cation. Based on earlier work by Wilkinson[252] in which a 1,5-binding mode was ascribed to the homologous 8-membered cycloocta-1,3-5-triene complex, Lewis concluded that the likely structure for the Co(I) complex formed upon hydride abstraction from triphenylmethane was **419**, in which the cycloheptatriene ligand adopts a 1,5-binding mode with a non-coordinated double bond situated between two coordinated olefins. Upon aqueous workup, the residual trityl cation was assumed to react with water to generate an acidic proton, which then protonates the cycloheptadiene complex **419** at the unbound olefin to generate **420** (Pathway A, Scheme **4.22**).

More recent reports by Salzer[253] on the same system indicate that the cyclohepta-1,3,5-triene ligand actually adopts the η^4- 1,3-binding mode when coordinated to CpCo(I) and that protonation of this complex at room temperature (Scheme **4.23**) generates the expected fully conjugated CpCo(III) η^5-cycloheptadienyl product **422** exclusively.

Scheme 4.23



421, 38%

422, 78%

Lewis offered no additional evidence to discount the alternate possibility that the conjugated complex **422** was the product isolated from the reaction of **417** with trityl cation. Both complexes **420** and **422** would be expected to have nine protons distributed amongst five distinct non-cyclopentadienyl chemical environments; since the complete

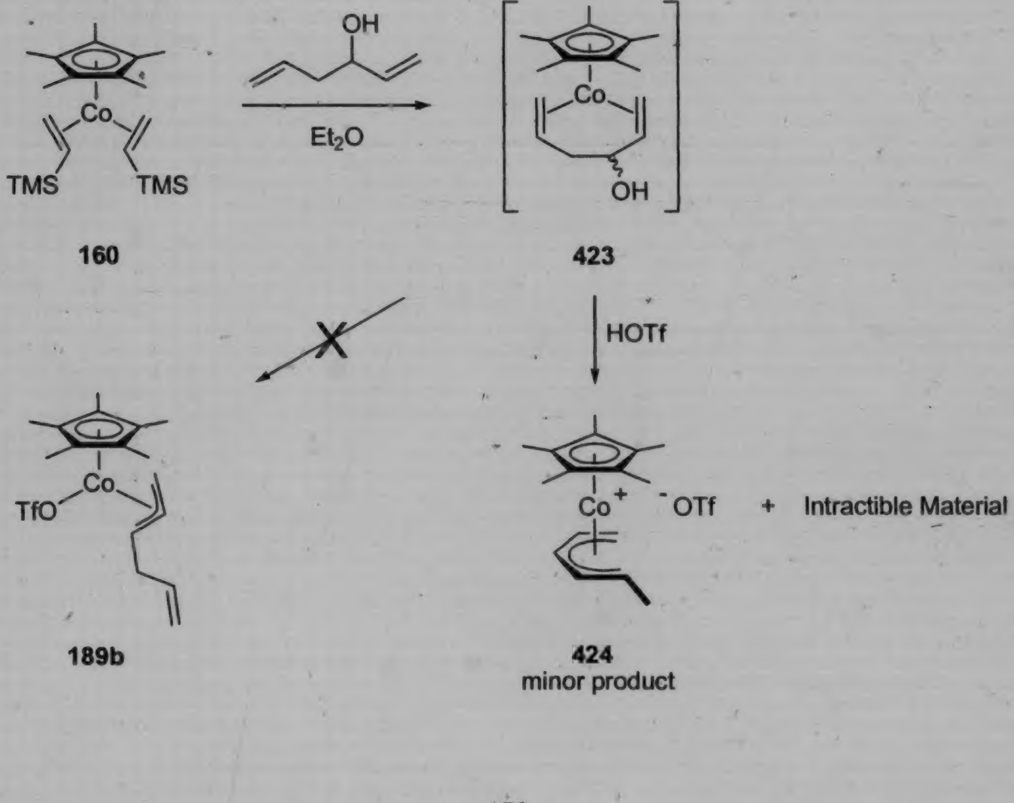
NMR data were omitted from the manuscript, the actual identity of the product isolated by Lewis remains incompletely defined, although it is most likely that it was η^5-cycloheptadienyl complex **422** that was, in fact, isolated (pathway B of Scheme **4.22**).

Section 2: Results and Discussion

*Part D: Synthesis of Cp*Co(III) Pentadienyl Complexes*

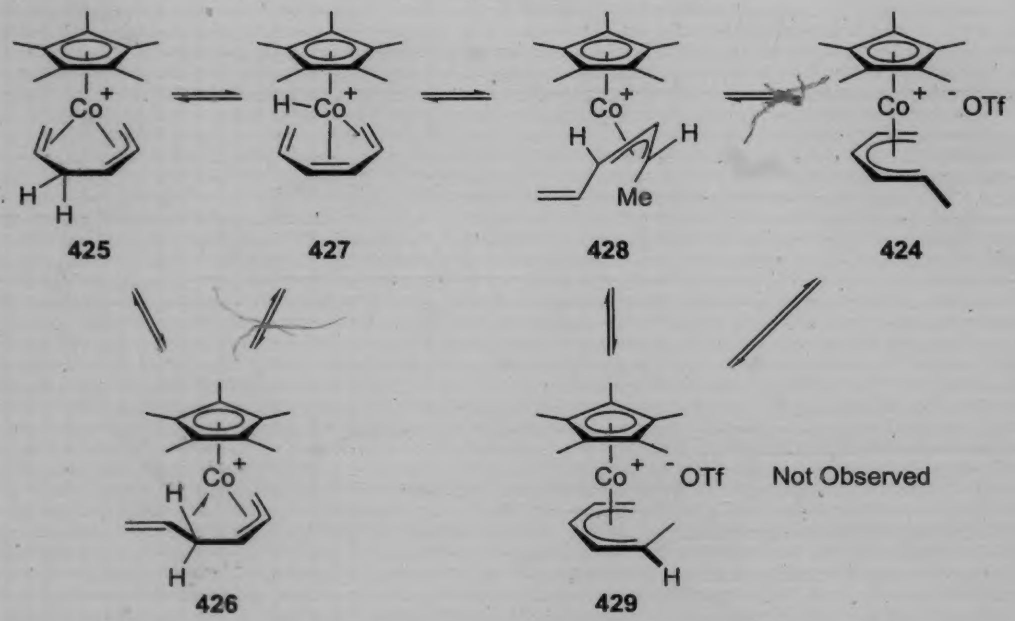
In our earliest attempts to synthesize an allyl-substituted η^3-allyl complex **189b**, hydroxyl-substituted diene complex **423** was formed *in situ* by exchange from **160** and then protonated with triflic acid. Although the reaction yielded mostly unidentified decomposition products to the exclusion of **189b**, a small amount of what appeared to be the 1-methylpentadienyl complex **424** was detected as a minor product in the mixture.

Scheme 4.24


Co
TMS
TMS
160
OH
Et₂O
Co
OH
423
HOTf
Co
TfO
189b
Co⁺
⁻OTf
+ Intractible Material
424
minor product

Although **424** was not the desired product from the oxidative addition, its formation was not entirely surprising. The η^3,η^2-allyl olefin complex **425** (Scheme **4.25**) is the anticipated immediate product from C-O activation of **423**, although it is quite possible that the agostic allyl complex **426** also lies on the reaction pathway. In either event, the olefin moiety cannot remain bound to the metal during the β-hydride elimination from **425** (Scheme **4.25**) without exceeding an 18-electron count at the metal. One consequence of this temporary olefin coordination (or the intermediacy of agostic allyl complex **426**) is that it predisposes activation of only one of the two possible β-hydrides; this in turn leads to a single cationic Co(III) hydride diene complex **427**, with the diene moiety in the more common s-*cis* configuration. Hydride re-insertion furnishes the allyl intermediate **428** bearing both substituents with *anti* stereochemistry; the

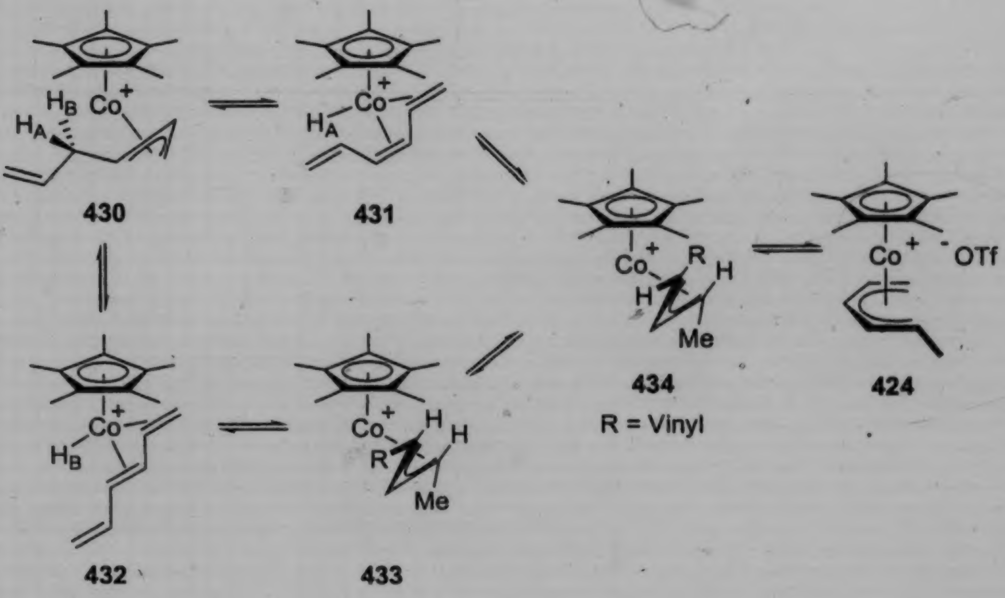
Scheme 4.25



observed product **424** is accessed from **428** via a series of allyl isomerization steps in which the methyl group adopts the *syn* stereochemistry; the *anti* η^5-U pentadienyl complex **429**, also accessible from **428**, is notably absent from the product mixture. If **429** indeed forms, it can also isomerize to **424** via a series of allyl ligand isomerization steps.

Even if the oxidative addition does form some of the target allyl complex **189b**, this species could also proceed to **424** via a series of rearrangements not unlike those proposed for the formation of **190** in Chapter 2. In one possible pathway (Scheme **4.26**), the weakly coordinated triflate counterion dissociates from the complex **189b** while the allyl ligand is in the favored *syn-exo* configuration. In this case, either of the two available β-hydrides in intermediate **430** may then be activated to afford a cationic

Scheme 4.26



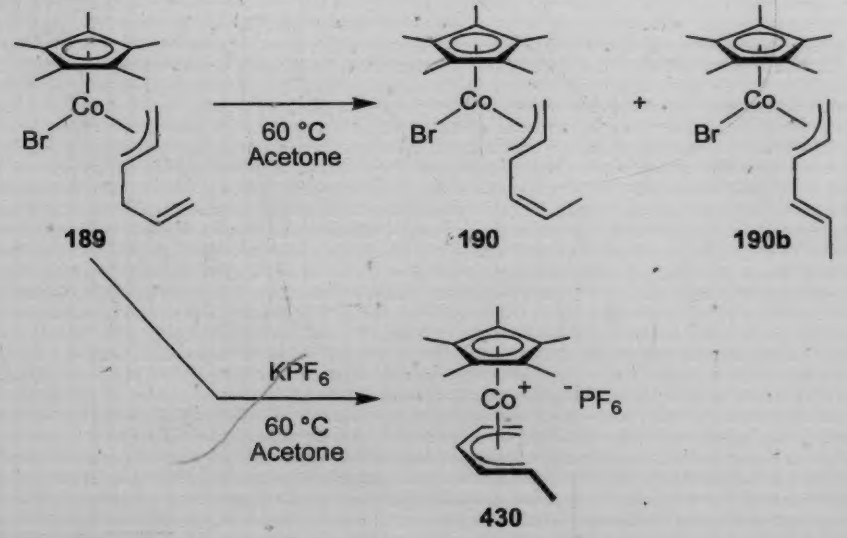
Co(III) hydride intermediate bearing a diene ligand in the *s*-trans configuration. Depending on which hydride is activated, the pendant terminal vinyl group with either be *cis* (**431**) or *trans* (**432**) to the coordinated terminal vinyl group.

In either case, a subsequent hydride re-insertion furnishes an intermediate allyl complex (**433** or **434**), which exhibits an *endo* configuration with the methyl group *syn* to the central proton; this *syn* stereochemistry will translate directly into the *trans* stereochemistry of the methyl group of **424**, barring a further isomerization process. If H_B was the hydride activated in intermediate **430**, the allyl intermediate **433** is formed subsequently, and must isomerize to **434** in order to adopt the η^5-U configuration of the ultimate product **424**; this is likely accomplished via the η^1-allyl pathway (e.g. Scheme **2.21**) normally associated with this isomerization.

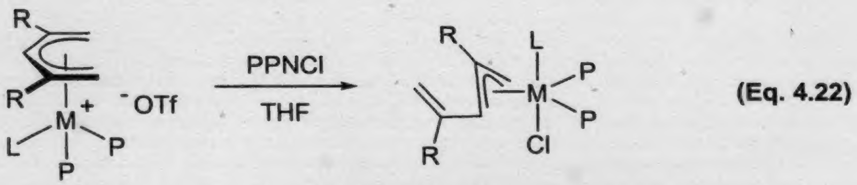
Of course, **189b** might also access **424** by simply isomerizing to the corresponding *anti* configuration before dissociating the triflate ion to generate **425** or **426**; from here, the formation of **424** would proceed as outlined in Scheme **4.25**.

A similar isomerization process is implicated in the production of small amounts of the conjugated complex **190** in the formation (by oxidative addition) of **189** reported earlier in this thesis (Chapter 2, Equation **2.33**). To test the ability of complex **189** to isomerize thermally to a *conjugated* η^3-pentadienyl complex, **189** was heated at 60°C in acetone for several hours (Scheme **4.27**). Upon product isolation, a mixture of compounds **190** and **190b** were obtained in high yield, to the complete exclusion of starting material. Not surprisingly, the *trans* isomer **190b** was slightly favored over the *cis* isomer **190**; this suggests a further thermodynamic isomerization process occurs after the non-coordinated double bond moves into conjugation as the *cis* isomer is expected to be the immediate product from the double bond migration pathway.

Scheme 4.27



Such isomerization processes find precedent in the literature. Bleeke has reported in detail the solution dynamics and isomerization reactions of M(I) and M(III) complexes of Group 9 transition metals,[174,254-259] as well as related chemistry involving Fe,[260-264] Ru,[265,266] Mn,[267-269] and Re.[269-271] Of particular interest, Bleeke reports that in the presence of the weakly coordinating triflate counterion, the Rh(III)[255] and Ir(III)[259] complexes **431** – **436** exist as 18-electron η^5-pentadienyl cations, but upon treatment with the more nucleophilic counterion such as chloride, a neutral inner-sphere η^3-complex is preferred (Equation **4.22**).

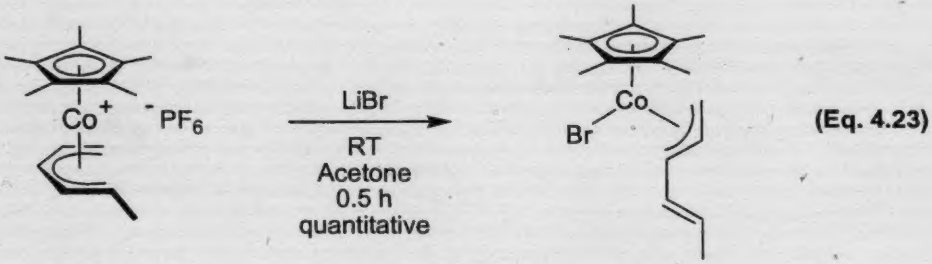


431-436

437: M = Rh, L = R = Me, P = PMe_3, 77%
438: M = Rh, L = R = Me, P = PEt_3, 80%
439: M = Ir, L = R = H, P = PEt_3, 73%
440: M = Ir, L = H, R = Me, P = PEt_3, 77%
441: M = Ir, L = Me, R = H, P = PEt_3, 80%
442: M = Ir, L = R = Me, P = PEt_3, 84%

With these observations in mind, allyl complex **189** was again heated in acetone under identical conditions as before, with the exception that KPF_6 was also present in the reaction medium to trap the bromide ion as an acetone-insoluble KBr precipitate. Under these conditions, the Cp*Co(III) η^5-pentadienyl complex **430** was formed in good yield (Scheme **4.27**). Interestingly, the product contains no detectable amounts of the *cis* (*endo)* isomer, which would correspond to the *cis*-η^3-precursor **190**.

The reversibility of this reaction was also tested; a slight excess of lithium bromide was added to an acetone solution of η^5-pentadienyl complex **430** and within 10 minutes at room temperature allyl complex **190b** was isolated in good yield as the only observable isomer (Equation **4.23**).

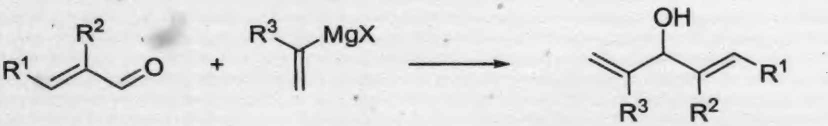


430 **190b**

Interestingly, allowing the reaction to proceed for longer reaction times resulted primarily in the formation of an unidentified blue decomposition product. It is possible that the excess bromide ion present, along with the moderately co-ordinating solvent, was sufficient to promote a catalytic decomposition of the allyl **190b** via homolysis of a stabilized η^1-allyl intermediate, although no further experiments were performed to assess this possibility.

The synthesis of Cp*Co(III) 1-methylpentadienyl hexafluorophosphate from the Cp*Co(III) allyl bromide precursor **189** was of specific interest because the requisite starting material was readily available, as a result of its use in the [3+2+2] chemistry described in Chapter 2. This method, however, is not a *general* pathway for the synthesis of η^5-pentadienyl complexes. Instead, a more general pathway was envisioned in which an organic pentadienyl fragment could be assembled in a small number of simple steps using well-established synthetic chemistry that could accommodate any number of substitution patterns. With a library of such organic precursors in hand, an ideal synthesis of Co(III) pentadienyl complexes then involves a one-step complexation process in which the pentadienyl ligand is installed in high yield from a ubiquitous source of half-sandwich cobalt(I).

The synthesis of 1,4-diene-3-ols by 1,2-addition of vinylmagnesium or vinyllithium reagents to α,β-unsaturated aldehydes is a well-established pathway to pentadienyl precursors. Indeed, simple ligand precursors such as **443**,[272] **444**,[272] and **445**[273] have all been reportedly synthesized is this manner (Equation **4.24**), often for use as substrates in traditional Nazarov cyclization chemistry.



(Eq. 4.24)

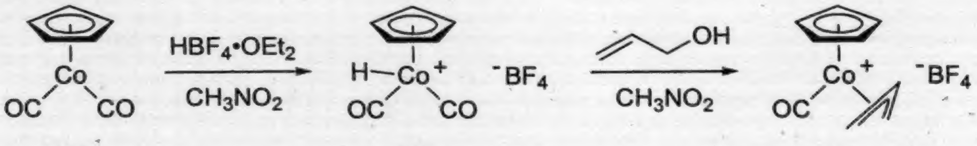
443: R^1 = Me, R^2 = R^3 = H
444: R^1 = R^3 = H, R^2 = Me
445: R^1 = R^2 = Me, R^3 = H
446: R^1 = R^2 = R^3 = Me
447: R^1 = Ph, R^2 = R^3 = Me

Because almost any pentadienyl substitution pattern can be accessed in this manner by judicious selection of the corresponding vinylmagnesium and enal precursors (many of which are commercially available), 1,4-pentadien-3-ols **443** – **445** were prepared in this manner. In addition, the trisubstituted substrates **446** and **447** were generously donated by Dr. Graham Murphy of Professor Fred West's group, who prepared them via the usual Grignard route for use in Nazarov chemistry.

With ready access to a selection of 1,4-pentadiene-3-ol substrates, a direct oxidative complexation approach was envisioned which employed a Cp*Co(I) half-sandwich precursor. In the early 1980's, Krivykh and co-workers[96,97] successfully prepared cationic allyl carbonyl complex **450** by protonation of a mixture of dicarbonyl **448** and allyl alcohol; the intermediacy of cationic hydride complex **449** was investigated by stepwise addition of acid, followed by propargyl alcohol (Scheme **4.28**). Although **449** was never isolated, bands arising at 2115 cm^{-1} and 2076 cm^{-1} in the infrared spectrum were attributed to this complex.

With this in mind, several attempts were made to prepare Cp*Co(III) pentadienyl complexes (via the Cp*Co(III) carbonyl η^3-pentadienyl intermediates) in an analogous manner. Unfortunately, these efforts were met only with frustration, yielding only

Scheme 4.28

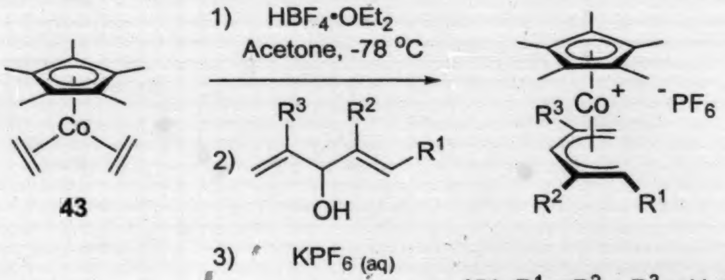


448 **449** **450**

unidentified decomposition products. It is reasonable to propose that the more electron-rich Cp* ligand renders the carbonyl ligands less labile, even upon protonation at the metal, so that protonation and decomposition of the organic substrate (perhaps by Nazarov-type chemistry) proceeds at a competitive rate.

The equally accessible Cp*Co(I) bis(ethylene) complex **43** appeared to be a much more likely alternative source of Co(I), owing to the greater lability of the less π-acidic ethylene ligands. Brookhart[274,275] previously demonstrated the low-temperature protonation of Cp*Co(I) bis(ethylene) **43** to form a cationic Cp*Co(III) ethylene ethyl complex, which exhibited a relatively strong agostic interaction. Given the tolerance of the Cp*Co template for strong acid, conditions were sought for a general, high-yielding protocol for the transformation of **43** into a family of Cp*Co(III) pentadienyl complexes; Etkin[95] had previously prepared the unsubstitued Cp*Co(III) allyl triflate **44** using this strategy (Equation **2.3**), but attempts by Etkin[94] to prepare substituted analogues in the same way were met with frustration.

The reaction was first probed using the commercially available parent 1,4-pentadien-3-ol (Equation **4.25**). In initial trials, the alcohol was added to a cold solution of bis(ethylene) complex **43** prior to protonation, but in later reactions the protonation was conducted first, before addition of alcohol; the point at which the alcohol was added did not seem to profoundly affect the yield of **451**. Acetone, THF, and dichloromethane were assayed as solvents, with the best results occurring in acetone.



(Eq. 4.25)

451: $R^1 = R^2 = R^3 = H$, 67%
430: $R^1 = Me$, $R^2 = R^3 = H$, 75%
452: $R^2 = Me$, $R^1 = R^3 = H$, 54%
453: $R^1 = R^2 = Me$, $R^3 = H$, 59%
454: $R^1 = R^2 = R^3 = Me$, 30%

This protocol was extended to a small range of substituted pentadienols **443** – **446**; complexes **430** and **451** – **454** were obtained in good to moderate yield. The reaction was less tolerant of the more highly substituted pentadienols. It may be that the steric bulk of these substrates impedes coordination to the metal center. In addition, the more highly substituted pentadienols are expected to form cations more readily upon protonation at oxygen, and it may be that the more substituted substrates are those more prone to undergo a competitive Nazarov cyclization. The bulky trisubstituted phenyl-bearing alcohol **447** failed in all attempts to furnish clean pentadienyl complex; of all substrates used, this dienol should give rise to the most stabilized carbocation upon protonolysis of the hydroxy group and thus is perhaps the most prone to the competing Nazarov pathway.

In all cases, the initially-formed Co(III) pentadienyl complexes were converted by simple counterion metathesis to the water-insoluble hexafluorophosphate salts, which were purified by silica gel chromatography and subsequent crystallization by pin-hole diffusion; several of the complexes yielded crystals suitable for X-ray diffraction study. However, repeated efforts to grow X-ray quality crystals of the parent complex **451** were met only with frustration and no crystallographic data for any half-sandwich Co *unsubstituted* pentadienyl complex are available in the literature. Some comparative ^{13}C and ^{1}H NMR data for the pentadienyl complexes are summarized in Tables **4.1** and **4.2** respectively, as few examples of this family of complexes have been previously characterized.

Table 4.1: Comparative ^{13}C NMR Spectroscopic Data for Cp*Co(III) Pentadienyl Hexafluorophosphate Salts in CH_2Cl_2-d_2

	451 parent	**430 1-Me**	**452 2-Me**	**453 1,2-Me**	**454 1,2,4-Me**
C1	65.5	84.9	61.1	76.4	79.1
C2	100.6 or 100.4[a]	100.4[a]	114.0	111.9	111.0
C3	100.0	95.5	98.3	96.6	95.1
C4	100.6 or 100.4[a]	100.4[a]	86.9	99.4	112.1
C5	65.5	64.5	67.5	66.7	61.8

[a] The resonances arising from carbons 2 and 4 could not be unambiguously distinguished from one another in compounds **430** and **451**, owing to the close proximity of the signals.

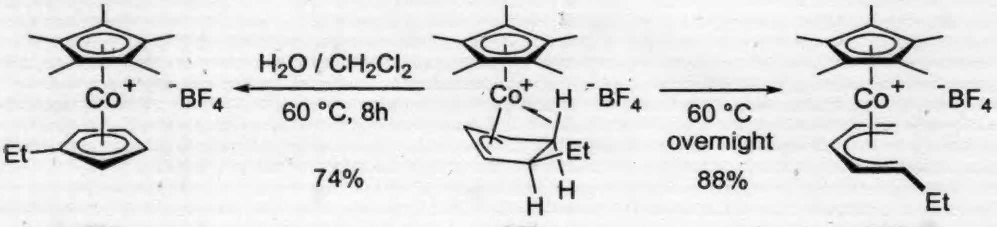
Table 4.2: Comparative ^{1}H NMR Spectroscopic Data[a] for Cp*Co(III) Pentadienyl Hexafluorophosphate Salts in CH_2Cl_2-d_2

	451 **parent**	**430** **1-Me**	**452** **2-Me**	**453** **1,2-Me**	**454** **1,2,4-Me**
$\mathrm{H1}_{anti}$	1.98	2.37	1.68	1.71	1.77
$J_{\mathrm{H1}anti\text{-}\mathrm{H2}}$	12.4 Hz	12.1 Hz	-	-	-
$J_{\mathrm{H1}anti\text{-}\mathrm{H1}syn}$	2.8 Hz	-	3.4 Hz	-	-
$\mathrm{H1}_{syn}$	3.50	-	3.22	-	-
$J_{\mathrm{H1}syn\text{-}\mathrm{H2}}$	9.7 Hz	-	-	-	-
$J_{\mathrm{H1}syn\text{-}\mathrm{H1}anti}$	2.8 Hz	-	3.4 Hz	-	-
H2	5.35	5.32	-	-	-
$J_{\mathrm{H2}\text{-}\mathrm{H1}anti}$	12.4 Hz	12.1 Hz	-	-	-
$J_{\mathrm{H2}\text{-}\mathrm{H1}syn}$	9.7 Hz	-	-	-	-
$J_{\mathrm{H2}\text{-}\mathrm{H3}}$	6.9 Hz	6.9 Hz	-	-	-
H3	6.52	6.46	6.40	6.39	6.34
$J_{\mathrm{H3}\text{-}\mathrm{H2}}$	6.9 Hz	6.9 Hz	-	-	-
$J_{\mathrm{H3}\text{-}\mathrm{H4}}$	6.9 Hz	6.9 Hz	7.0 Hz	7.3 Hz	-
H4	5.35	5.18	5.31	5.07	-
$J_{\mathrm{H4}\text{-}\mathrm{H5}anti}$	12.4 Hz	11.9 Hz	12.0 Hz	12.2 Hz	-
$J_{\mathrm{H4}\text{-}\mathrm{H5}syn}$	9.7 Hz	9.5 Hz	9.6 Hz	10.0 Hz	-
$J_{\mathrm{H4}\text{-}\mathrm{H3}}$	6.9 Hz	6.9 Hz	7.0 Hz	7.3 Hz	-
$\mathrm{H5}_{anti}$	1.98	1.97	2.09	2.35	2.07
$J_{\mathrm{H5}anti\text{-}\mathrm{H4}}$	12.4 Hz	11.9 Hz	12.0 Hz	12.2 Hz	-
$J_{\mathrm{H5}anti\text{-}\mathrm{H5}syn}$	2.8 Hz	3.4 Hz	3.0 Hz	3.5 Hz	4.2 Hz
$\mathrm{H5}_{syn}$	3.50	3.39	3.57	3.45	3.16
$J_{\mathrm{H5}syn\text{-}\mathrm{H4}}$	9.7 Hz	9.5 Hz	9.6 Hz	10.0 Hz	-
$J_{\mathrm{H5}syn\text{-}\mathrm{H5}anti}$	2.8 Hz	3.4 Hz	3.0 Hz	3.5 Hz	4.2 Hz

[a] In some cases ^{4}J couplings of small magnitude ($\leq$ 1.0 Hz) could be observed in the pentadienyl systems. These couplings, where observed, are included in the experimental section, but are omitted here for clarity.

The orange-red Cp*Co(III) pentadienyl complexes were all stable to exposure to air and moisture, as well as silica-gel chromatography. Despite this, several samples stored for prolonged periods (6 months) on the bench at room temperature exhibited evidence for the formation of a very small amount (less than 5% of total) of the corresponding cobaltocenium species. A possible mechanism for this cobaltocenium product involves a cyclization to an agostic allyl species, followed by elimination of a hydrogen molecule. Spencer has previously demonstrated[201] that cationic Cp*Co(III) agostic allyl complexes (i.e **358**) will form either pentadienyl products or cyclopentadienyl products, depending on the amount of moisture present; water may accelerate the formation of cobaltocenium **455** by facilitating hydrogen loss by acting as an external base (Scheme **4.29**).

Scheme 4.29



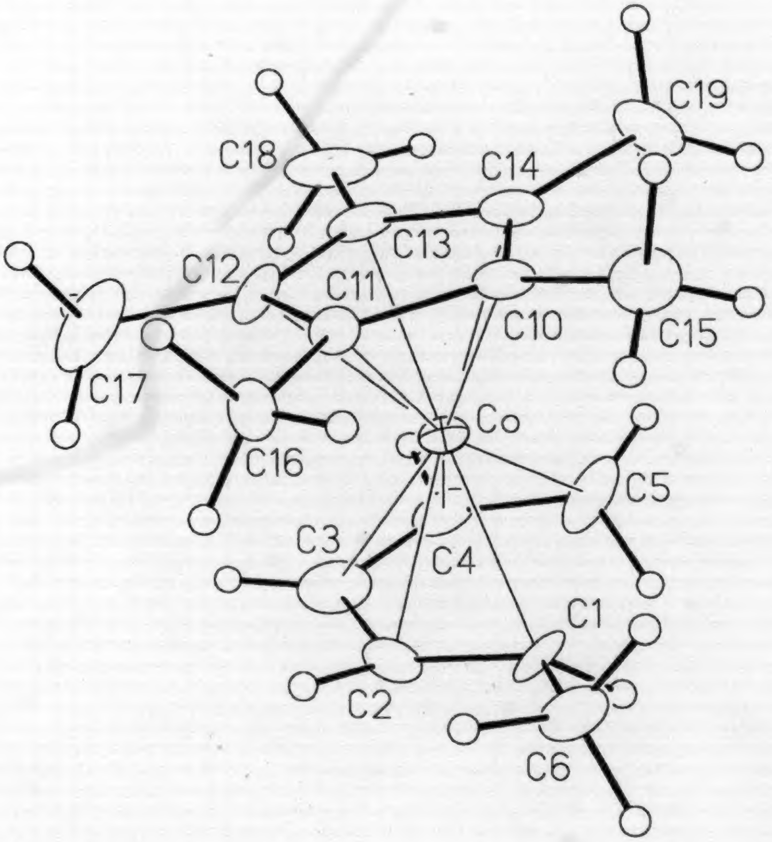
455 **358** **359**

The possible reversibility of the carbon-carbon bond activation event (*i.e.* **359** to **358**) was not considered by Spencer, and is otherwise unknown in the literature. It remains unclear whether the slow cyclization of pentadienyl complexes on the bench under ambient conditions is accelerated by the presence of adventitious atmospheric moisture.

The solid-state structures of several of the Cp*Co(III) pentadienyl complexes were determined by X-ray crystallography; these structures are summarized on the following pages. The structure of methylpentadienyl complex **430** reveals an interesting asymmetry about the pentadienyl fragment in which the C2-C3 bond is significantly longer than the C3-C4 bond. In fact, the C2-C3 bond is of a length normally associated with a single bond. As such, the pentadienyl ligand, at least in the solid state, appears to approach an η^2,η^3-bonding mode. Spencer has reported the crystal structure for a related 1-ethylpentadienyl complex, crystallized as the tetraphenylborate salt from **359** (Scheme **4.29**),[172] and a similar asymmetry is present in the crystal structure of this molecule as well. None of the other three structures, however, show any distortion from typical pentadienyl complex bond lengths.

One other difference between the crystal structure of 1-methyl substituted complex **430** and the other Co(III) pentadienyl complexes **452** – **454** is significant. The plane defined by the quaternary carbons of the Cp* ring in **430** is nearly coplanar to the plane defined by the five coordinated pentadienyl carbons; the dihedral angle between these planes is 1.4(2)°. In each of the other three cases, this dihedral angle is close to 10°, with C3 of the pentadienyl fragment lying furthest from the plane defined by the Cp*. Pentadienyl complex **430** differs from the other examples in that it is the only example without a substituent on C2 (or C4) of the pentadienyl fragment. It may be that a substituent in this position imposes a subtle influence on the structure, which ultimately results in the observed deviation from co-planarity; this structural difference may in turn be responsible for the differences in chemistry that are observed for complex **430**, when compared to the other pentadienyl complexes (*vide infra*). Of course, the solid-state structural differences in **430** may simply be a result of crystal packing forces and it is very possible that solution structure of **430** more closely resembles those of **452** – **454**.

Figure 4.2: ORTEP for Complex **430** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0423

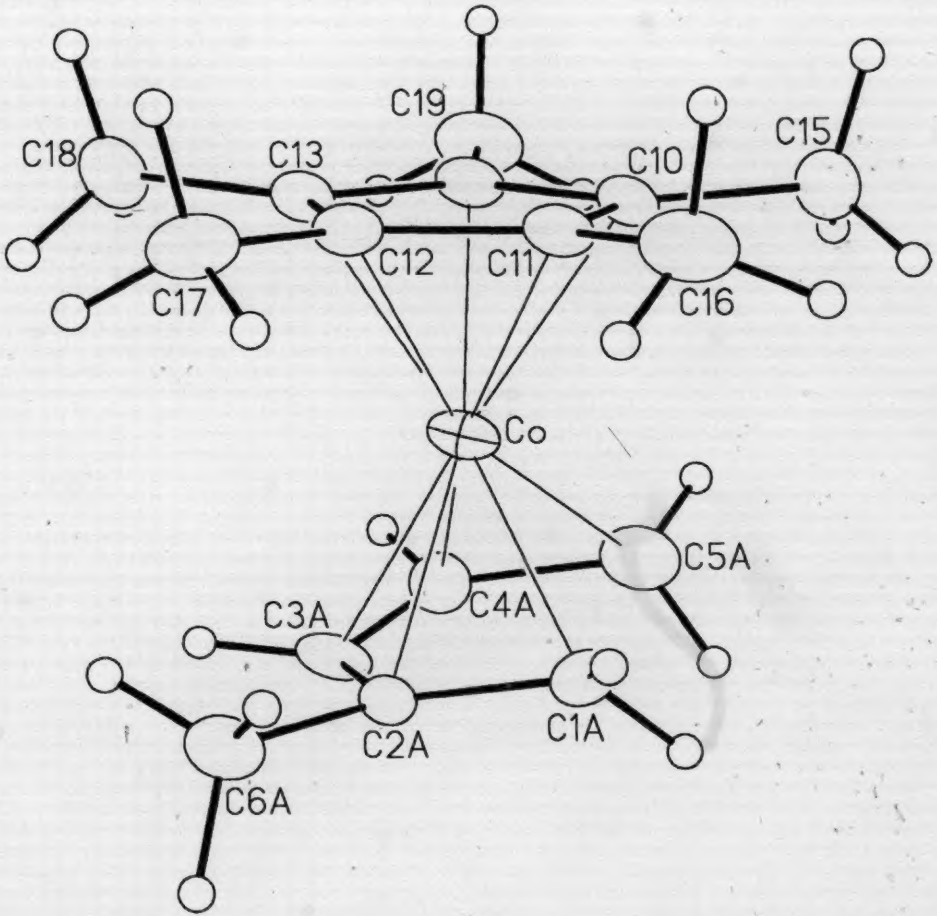

C19
C18
C14
C13
C12
C11
C10
C15
C17
Co
C16
C5
C3
C4
C1
C2
C6

Final Residuals: $R_1 = 0.0437$; $wR_2 = 0.1025$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C2, 1.373(12); C2-C3, 1.568(13); C3-C4, 1.389(18); C4-C5, 1.406(19); C1-C6, 1.499(5).

The dihedral angle between the planes defined by C10-C14 and C1-C5 = 1.4(2)°.

Figure 4.3: ORTEP for Complex **452** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0452

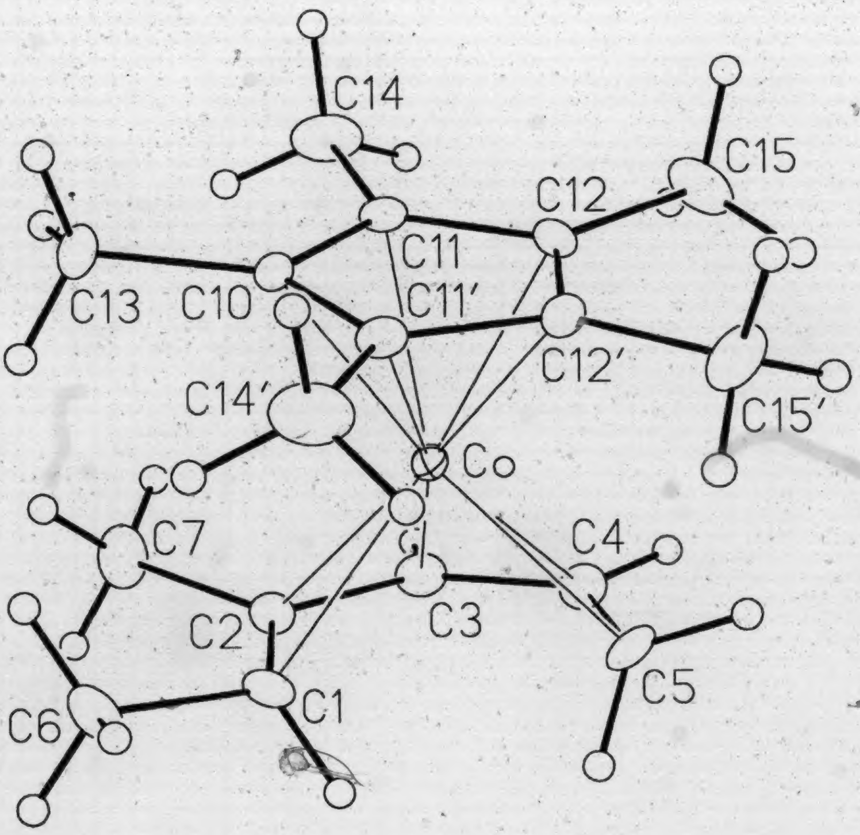

C19
C18
C13
C10
C15
C12
C11
C17
C16
Co
C5A
C3A
C4A
C2A
C1A
C6A

Final Residuals: $R_1 = 0.0438$; $wR_2 = 0.1257$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1A-C2A, 1.428(16); C2A-C3A, 1.429(15); C3A-C4A, 1.392(10); C4A-C5A, 1.526(11); C2A-C6A, 1.482(13).

The dihedral angle between the planes defined by C10-C14 and C1A-C5A = 11.90(19)°.

Figure 4.4: ORTEP for Complex **453** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0520

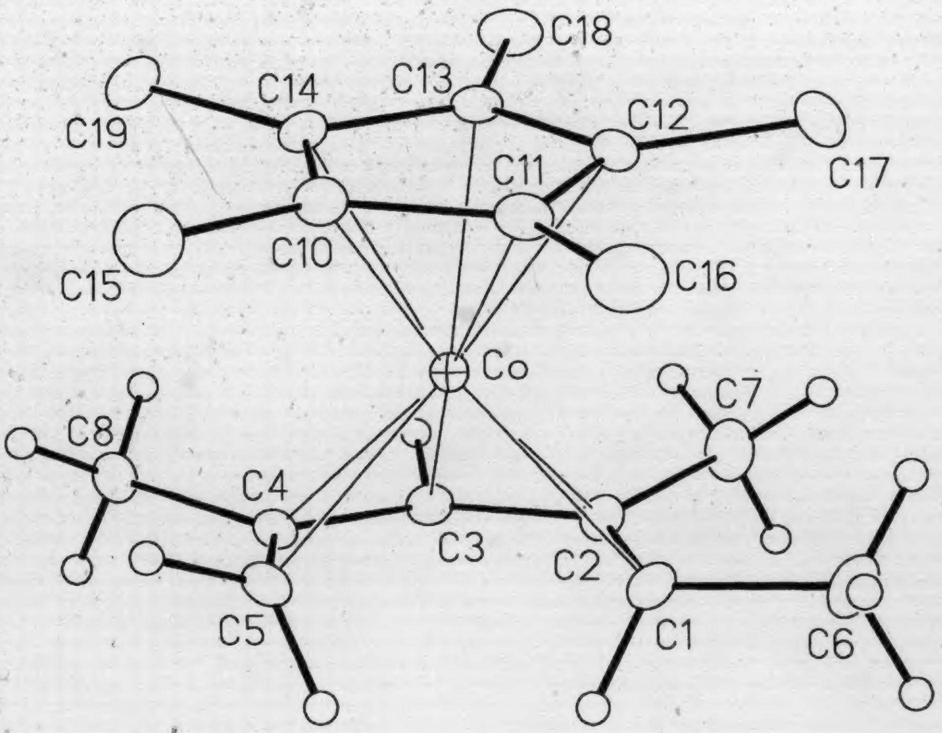

C14
C15
C12
C11
C13
C10
C11′
C12′
C14′
C15′
Co
C7
C4
C2
C3
C1
C6
C5

Final Residuals: $R_1 = 0.0514$; $wR_2 = 0.1490$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C2, 1.398(14); C2-C3, 1.430(10); C3-C4, 1.46(2); C4-C5, 1.378(14); C1-C6, 1.519(12); C2-C7, 1.517(12).

The dihedral angle between the planes defined by C10-C12 (including C11' and C12') and C1-C5 = 9.55(16)°.

Figure 4.5: ORTEP for Complex **454** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0570


C18
C14
C13
C12
C19
C11
C17
C10
C15
C16
Co
C7
C8
C4
C3
C2
C5
C1
C6

Final Residuals: $R_1 = 0.0410$; $wR_2 = 0.1322$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

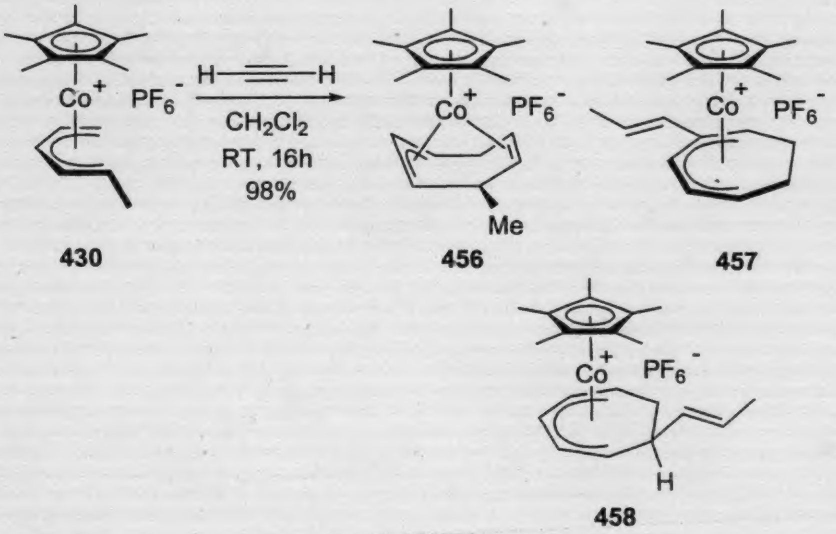
Selected Bond Distances (Å): C1-C2, 1.405(4); C2-C3, 1.426(3), C3-C4, 1.420(4); C4-C5, 1.418(3); C1-C6, 1.506(4); C2-C7, 1.508(3); C4-C8, 1.514(4).

The dihedral angle between the planes defined by C10-C14 and C1A-C5A = 10.28(17)°.

*Part E: Reactivity of Cp*Co(III) Pentadienyl Complexes with Alkynes – An Unprecedented Thermal [5+2] Cycloaddition Reaction.*

*1. Reactions of Cp*Co(III) 1-methylpentadienyl cation with acetylene*

The 1-methylpentadienyl complex **430** was the first such complex prepared in this study and was thus the first to be assayed for reactivity with alkynes. In early reactions, a dilute solution of **430** in either dichloromethane or acetone was saturated with acetylene and allowed to stand at room temperature overnight. Upon removal of solvent *in vacuo*, the major product species recovered in each case was neither the starting material **430**, nor the η^5-cycloheptadienyl product expected from a typical [3+2+2] cycloaddition reaction (Equation **4.26**).

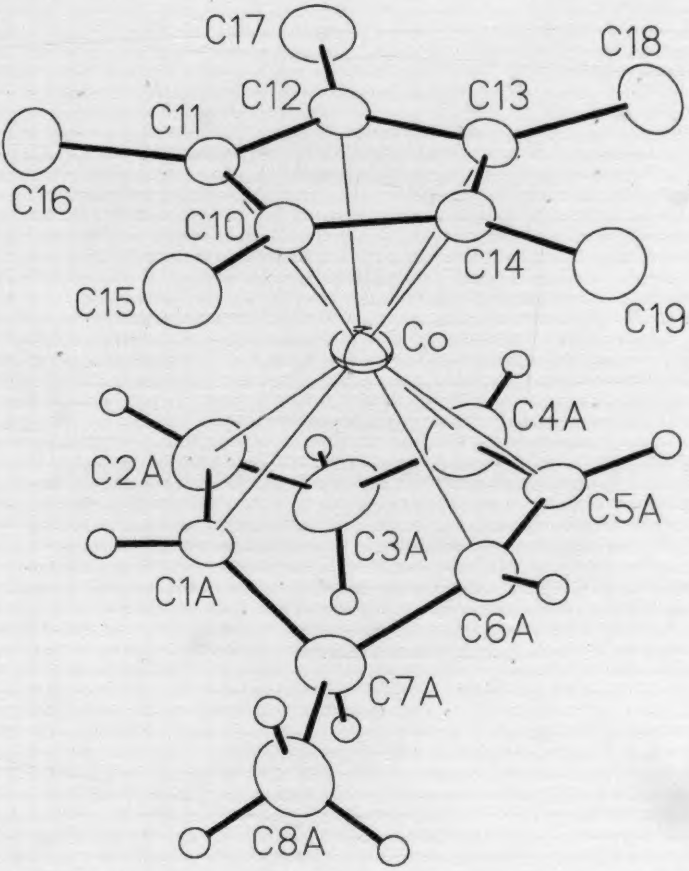


(Eq. 4.26)

Spectroscopic interrogation of the product mixture identified the major product as the unprecedented Cp*Co(III) η^3,η^2-cycloheptadienyl complex **456**. Also present, in small amounts (less than 5% each of total), were complexes **457** and **458**, which were identified on the basis of careful ^{1}H NMR analysis and GCOSY. These by-products could not be isolated or separated from the bulk product mixture and thus have not been completely characterized. Fractional crystallization of this mixture from a mixture of dichloromethane and ether, however, yielded analytically pure crystals of **456** which were suitable for X-ray crystallography.

The formation of η^3,η^2-complex **456** is likely mechanistically similar to the [3+2+2] cycloaddition, at least in the initial steps (Scheme **4.30**). Since the pentadienyl complex **430** is an 18-electron species, a coordination site must be vacated in order to accommodate the incoming alkyne. The apparently facile slippage to the η^3-configuration facilitates this process and, upon alkyne coordination, a cationic η^3-pentadienyl alkyne complex **460** is formed which is structurally similar to the η^3-allyl alkyne intermediate proposed in the [3+2+2] reaction (i.e. **92** Scheme **2.11**). In principle, either end of the pentadienyl fragment in **430** could decomplex, but given that **430** forms only η^3-allyl complex **190b** upon treatment with bromide (Equation **4.23**), it seems reasonable to propose that dissociation of the methyl-substituted end of the pentadienyl ligand is preferred. More evidence for this regioselectivity will be discussed later in this chapter.

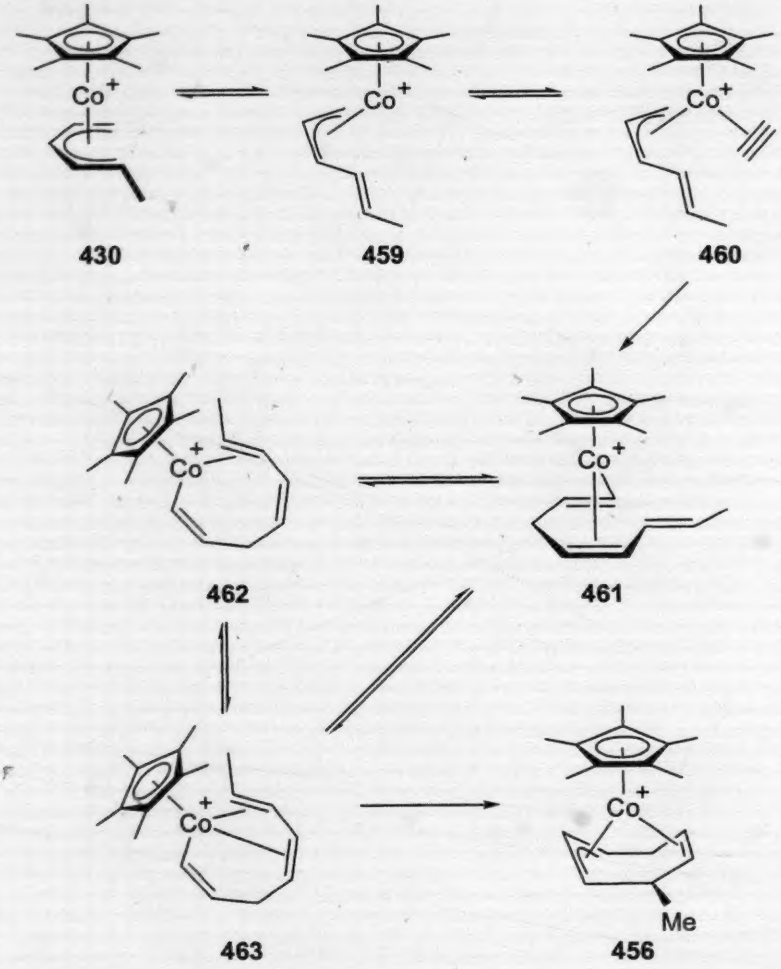
Figure 4.6: ORTEP for Complex **456** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0435


C17
C18
C12
C13
C11
C16
C10
C14
C15
C19
Co
C4A
C2A
C5A
C3A
C1A
C6A
C7A
C8A

Final Residuals: $R_1 = 0.0617$; $wR_2 = 0.1929$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1A-C2A, 1.393(6); C1A-C7A, 1.476(5); C2A-C3A, 1.590(8); C3A-C4A, 1.396(7); C4A-C5A, 1.426(6); C5A-C6A, 1.372(5); C6A-C7A, 1.508(4).

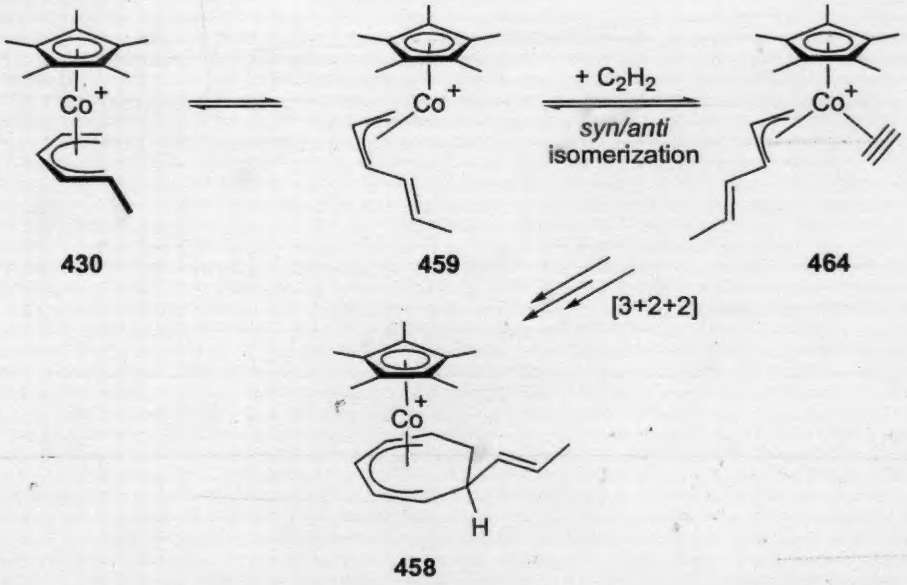
Scheme 4.30



Upon coordination, the alkyne fragment then inserts into the carbon-metal bond at one terminus of the allyl ligand. Mechanistically, the exact details of this insertion are still somewhat hazy, but have been discussed at some length by Dzwiniel.[17] It is possible that the insertion proceeds directly from the η^3-allyl intermediate **460**. On the other hand, it is also possible that the allyl further dissociates to an η^1-binding mode; the electron deficient Co(III) η^1-allyl complex may be further stabilized by coordination of a second equivalent of alkyne or by coordination of the orthogonal pair of π electrons in the existing alkyne ligand.[276]

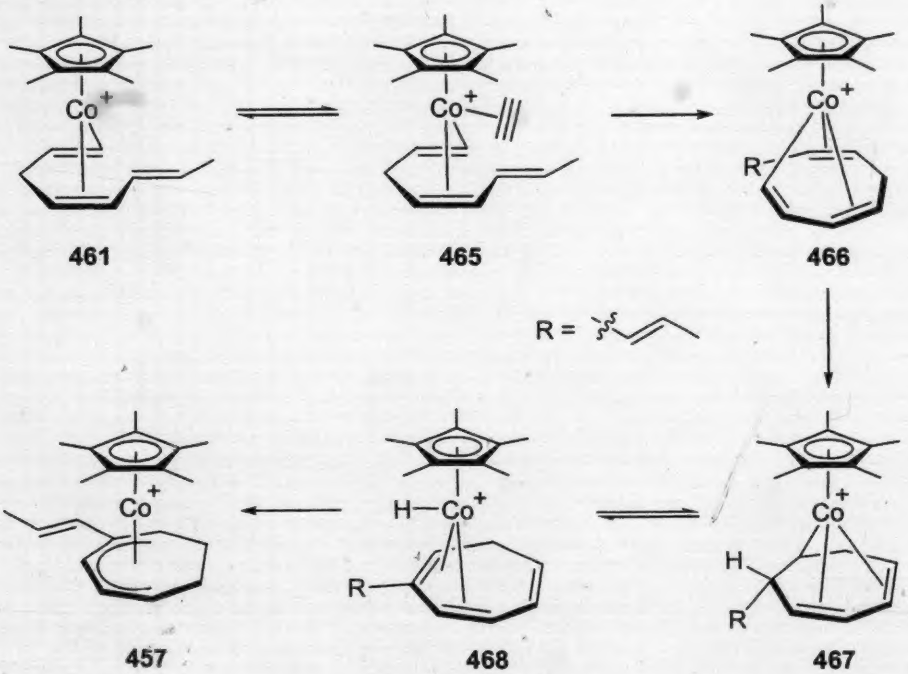
The formation of the two observed by-products is easily rationalized based on the known and expected chemistry of Co(III) η^3-allyl complexes. Vinyl-substitued cycloheptadienyl complex **458** is the expected product from a normal [3+2+2] cycloaddition if the starting material were to first isomerize to the *syn*, *exo* isomer of the η^3-pentadienyl cation (Scheme **4.31**). In the presence of acetylene, it is plausible that some amount of this η^3-pentadienyl complex might exist in solution. Indeed, a high concentration of acetylene may promote formation of this isomer: isomerization to the *syn* isomer from *anti*-η^3-pentendienyl complex **459** must involve formation of an η^1-pentadienyl intermediate, which could be stabilized by coordination of a second equivalent of acetylene.

Scheme 4.31



The formation of the isomeric **457** is somewhat more interesting (Scheme **4.32**). Assuming, as before, that the methyl-substituted terminus of the pentadienyl ligand dissociates to permit alkyne coordination and migratory coupling, σ-vinyl olefin intermediate **461** is subsequently formed. In the presence of a large excess of acetylene, however, a second equivalent of alkyne could coordinate to the 16-electron intermediate competitively with the re-coordination of the pendant vinyl group originating from the pentadienyl ligand, giving intermediate **465**. This second alkyne fragment can then insert to generate the acyclic triene complex **466**. This process is analogous to the expected [3+2+2] cycloaddition reaction proposed to proceed from the *anti* isomer of a substituted allyl.

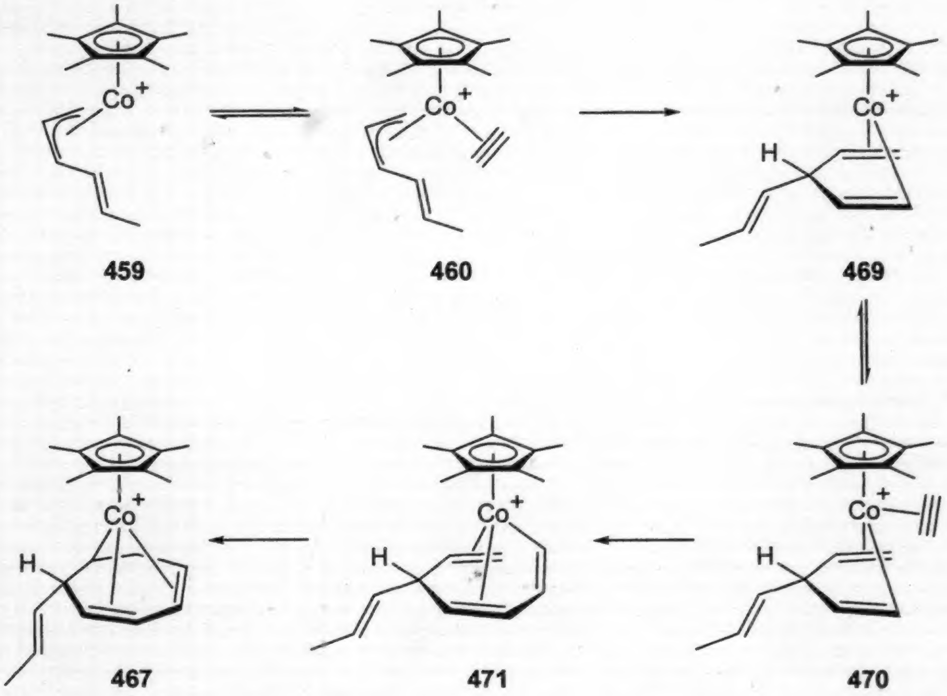
Scheme 4.32



A third migratory insertion reaction would close the seven-membered ring, affording the η^1,η^4-complex **467**; since it has been previously established that substituents in the *syn* position at the allyl terminus are situated on the same face of the ring as the metal in the analogous [3+2+2] chemistry, it is reasonable to assume that the cyclization event places this pendant vinyl substituent on the opposite face of the ring. The observed cycloheptadienyl by-product **457** then arises by activation of the β-hydride, followed by reinsertion.

For the formation of **178**, the regiochemistry of the first migratory insertion reaction is ultimately inconsequential. If it is the more substituted end of the allyl

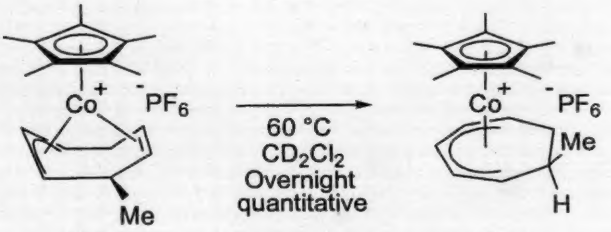
Scheme 4.33



fragment that forms the new carbon-carbon bond, the vinyl olefin intermediate **469** is formed (Scheme **4.33**). Further alkyne coordination and insertion would lead to intermediate **471** and the eventual cyclization event also affords the η^1,η^4-intermediate **467**.

Unfortunately, the minor products **457** and **458** could not be removed chromatographically. The crystallization of **456** successfully afforded analytically pure X-ray quality material, but in low recovery. As such, the reaction conditions need to be further optimized to minimize the formation of **457** and **458**. It is possible that the competitive formation of **458** might be reduced by lowering the concentration of acetylene present, since intermediate **461** will proceed to the desired product **456** unless a second molecule of acetylene hinders recomplexation of the pendant end of the pentadienyl fragment (Scheme **4.32**). As well, isomerization to the undesired *syn,exo* allyl complex **464** might also be promoted by high acetylene concentrations. On the other hand, too low an acetylene concentration might slow the rate of the formation of **460** and ultimately **456** below a practical level. If the reaction requires several days to proceed to completion, some of the product **456** will isomerize to the conjugated η^5 complex **472** (*vide infra*); this is not a problem if **472** is the ultimate target molecule, but can be an issue if a clean preparation of only **456** is desired.

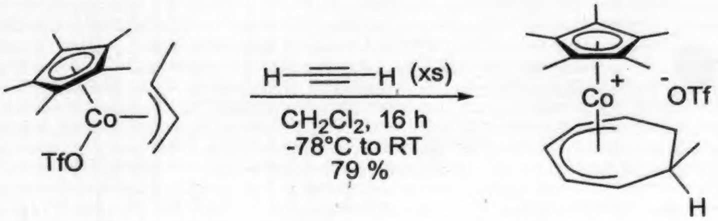
As expected based on the paucity of seven-membered "interrupted cyclopentadienyl" complexes (Part C of this chapter), η^3,η^2-complex **456** quantitatively converts to the conjugated η^5-cycloheptadienyl complex **472** upon heating overnight at 60°C in dichloromethane (Equation **4.27**). At lower temperatures, this conversion is much slower; an NMR sample of **456** left at room temperature over a weekend formed **472** as approximately 5% of the whole, and a sample stored at -20 °C was stable indefinitely. No quantitative investigation of the energetics of this isomerization was undertaken.



456 **472** **(Eq. 4.27)**

The isolation of non-conjugated cycloheptadienyl complex **456** under these reaction conditions is significant for several reasons. Since *conjugated* η^5-cycloheptadienyl complex **472** does not form until **456** is heated, this result confirms Dzwiniel's suggestion that Cp*Co(III) pentadienyl complexes are not competent intermediates in "anomalous" [3+2+2] reactions (Scheme **4.9**), as these reactions are conducted at low temperature and are never warmed beyond room temperature. In addition, the formation of **456** represents the first example of a potentially useful cobalt-mediated [5+2] cycloaddition reaction that is synthetically related to the more established [3+2+2] pathway.

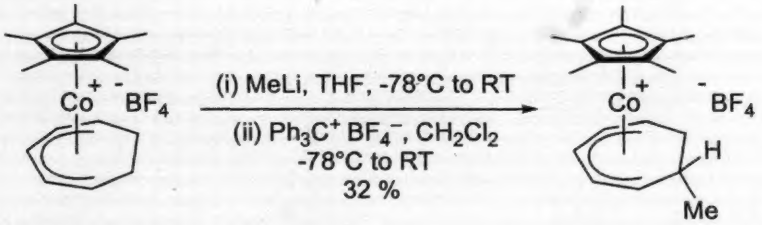
The isolation of a stable η^2,η^3-cycloheptadienyl complex also provides an important clue towards understanding a very early result obtained by Dzwiniel. From the [3+2+2] cycloaddition of acetylene with Cp*Co(III) crotyl triflate complex **45**, Dzwiniel isolated a single cycloheptadienyl product, which was tentatively assigned as **54**, with the methyl substituent on the same face of the ring as the metal (Equation **4.28**).


Co
TfO
H—≡—H (xs)
CH2Cl2, 16 h
-78°C to RT
79 %
Co +
- OTf
H

45 **54**

(Eq. 4.28)

As this was one of the first [3+2+2] reactions ever performed, the stereochemistry of this methyl substituent was not unambiguous and Dzwiniel was unable to harvest crystals of sufficient quality to permit an X-ray diffraction analysis. As such, Dzwiniel performed an independent synthesis of the other diastereomer **474**, starting from the parent complex **473**, by a nucleophilic methylation and a subsequent hydride abstraction (Equation **4.29**). Because the methylation is expected to be selective for the ring face opposite to the metal, Dzwiniel correctly assigned an *exo* stereochemistry to **474** and, by extension, the *endo* chemistry to **54**.


Co + - BF4
(i) MeLi, THF, -78°C to RT
(ii) Ph3C+ BF4−, CH2Cl2
-78°C to RT
32 %
Co +
- BF4
H
Me

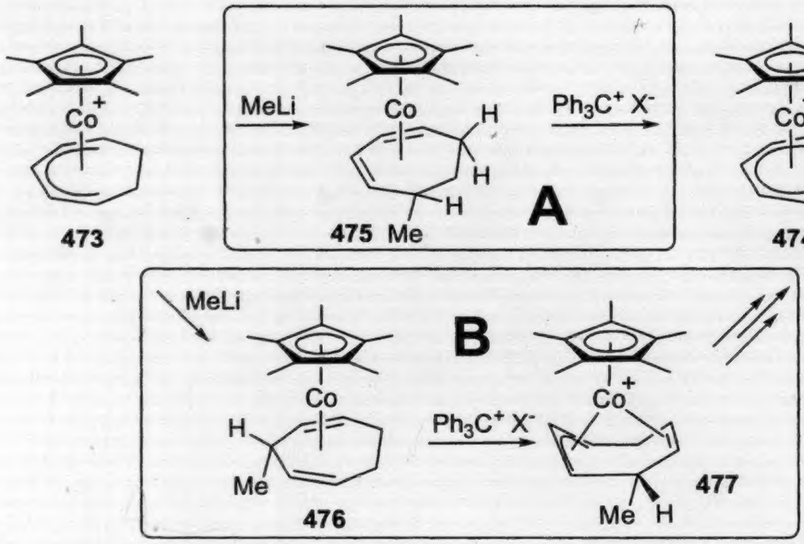
473 **474**

(Eq. 4.29)

Since Dzwiniel was seeking only a rapid synthesis of **474**, no isolation or characterization of the intermediate Co(I) methyl adduct was undertaken prior to hydride abstraction. Since the ultimate product of the sequence was determined to be η^5-

cycloheptadienyl complex **474**, Dzwiniel assumed that methylation occurred at a terminal carbon, and that the Co(I) intermediate was a conjugated Co(I) butadiene complex **475** (Scheme **4.34**, pathway A). More recent work (Chapter 2), however, has revealed that central-carbon methylation would be the anticipated *kinetic* result of the treatment of **473** with methyl lithium, affording the non-conjugated Co(I) diene intermediate **476**. This intermediate, however, can be reconciled with the observed hydride abstraction product **474** if the possible intermediacy of a Cp*Co(III) η^2,η^3-cycloheptadienyl **477** is considered (Scheme **4.34**, pathway B).

Scheme 4.34

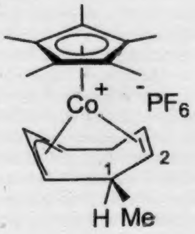
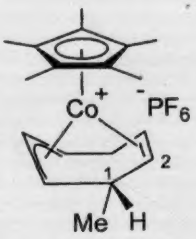


To test this hypothesis, unsubstituted cycloheptadienyl complex **475** was methylated under the conditions employed by Dzwiniel, with the exception that the product was filtered through alumina and isolated in order to render it suitable for NMR interrogation. As expected, the central carbon adduct **476** was, in fact, the major product with a minor (~ 10%) amount of terminal carbon adduct **475** present as well.

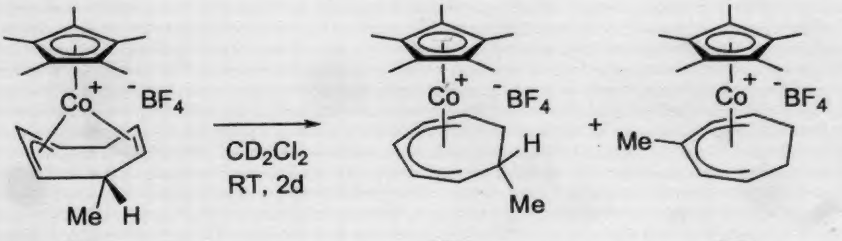
A low temperature NMR experiment was then conducted to probe for the intermediacy of a Cp*Co(III) η^2,η^3-cycloheptadienyl species in the hydride abstraction. A CD_2Cl_2 solution of the methyl adduct mixture was cooled to -78 °C and treated with a slight excess of triphenylcarbenium hexafluorophosphate. The ^{1}H NMR spectrum was immediately obtained at -80 °C, revealing complete conversion of the Co(I) complex **476** to η^3,η^2-cycloheptadienyl cation **477** (PF_6^- salt), the diastereomer of complex **456**. The NMR spectroscopy of complexes **456** and **477** is summarized in Table **4.3** for comparative purposes. As anticipated, the greatest differences in the ^{1}H NMR characteristics appear near the epimeric center. The chemical shift of H_1 is located a full ppm further downfield in complex **477**, and the adjacent protons (H_2 and H_3) are also significantly further deshielded (by ~ 0.7ppm) in this diastereomer.

The NMR sample was warmed rapidly to room temperature over a few minutes; even at room temperature η^3,η^2-complex **477** was persistent. Maintaining the solution for 48 hours at room temperature, however, resulted in complete conversion to Cp*Co(III) cycloheptadienyl complexes **474** and **479** (Equation **4.30**). It is therefore reasonable that Dzwiniel did not observe the tetrafluoroborate salt of **477** in his experiment, which was allowed to warm to room temperature overnight. It is indeed possible that Dzwiniel did not chromatograph and characterize his final product until several days afterwards, during

Table 4.3: Selected ^{1}H NMR Spectroscopic Data for Cp*Co(III) η^2,η^3-Cycloheptadienyl Hexafluorophosphate Salts **456** and **477** in CH_2Cl_2-d_2

	 **456**	 **477**
H1	2.40 $J_{H1\text{-}H2}$ = 5.5 Hz $J_{H1\text{-}H7}$ = 3.7 Hz $J_{H1\text{-}Me}$ = 6.9 Hz	3.44 $J_{H1\text{-}H2}$ = 7.7 Hz $J_{H1\text{-}H7}$ = 8.8 Hz $J_{H1\text{-}Me}$ = 7.3 Hz
H2	2.35	2.90
H3	2.77	2.84
H4	2.17	2.35
H4	3.22	3.21
H5	3.85	3.92
H6	3.20	3.40
H7	3.55	4.29
C1-C$\underline{H}_3$	1.47	0.87
Cp(C$\underline{H}_3$)$_5$	1.82	1.81

which time the isomerization of **477** may have proceeded to completion. Interestingly, Dzwiniel does not report the formation of isomeric **479**; it is possible that any of this product obtained by Dzwiniel was removed by crystallization prior to spectroscopic analysis.

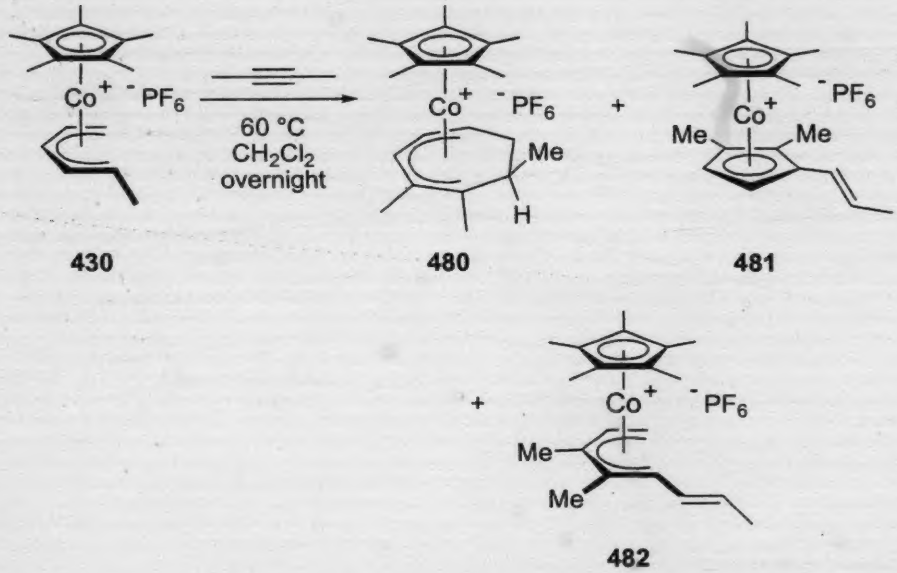


477 **474** **479**

(Eq. 4.30)

*2. Reactions of Cp*Co(III) 1-methylpentadienyl cation with substituted alkynes*

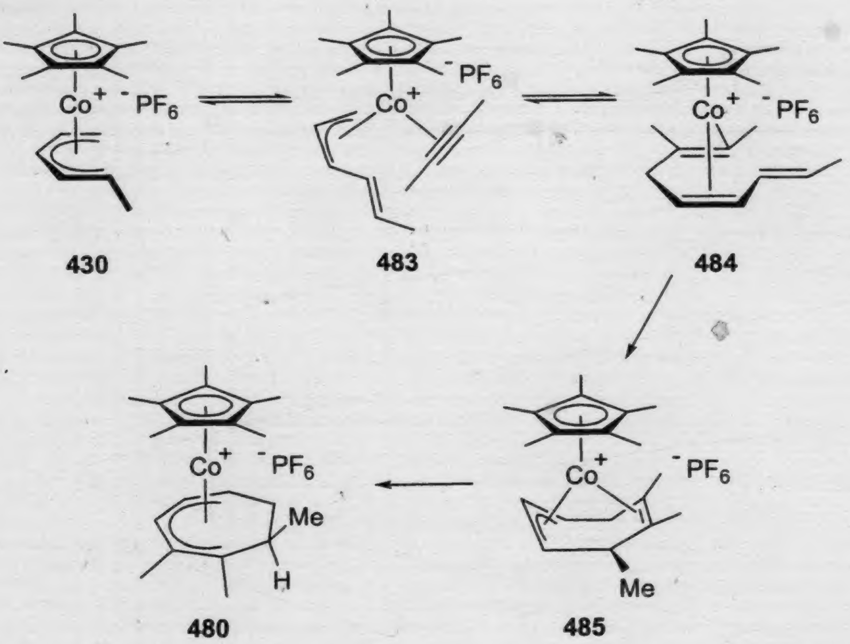
The reactivity **430** with substituted alkynes was also investigated. At room temperature, a solution of **430** and 2-butyne remained unchanged. The same mixture heated at 60 °C overnight, however, furnished of a mixture of three products of which Cp*Co(III) cycloheptadienyl complex **480** was identified as the major component (Equation **4.31**). The two minor components (each ~5% of the whole) were tentatively identified as complexes **481** and **482**; neither starting material **430** nor the anticipated η^3,η^2-cycloheptadienyl intermediate **485** were detected in the crude product matrix.



(Eq. 4.31)

Neither **481** nor **482** could be isolated from the major product and, as such, the characterization of these complexes is limited to ^{1}H NMR spectroscopy. Nonetheless, the formation of these complexes can be rationalized as a competitive departure from the anticipated pathway for the formation of **480**. Assuming that a single equivalent of 2-butyne is coordinated by the metal and subsequently coupled to the pentadienyl ligand, vinyl olefin intermediate **484** is expected. From this key intermediate, the reaction could proceed via seven-membered ring formation (as per Scheme **4.35**) to fashion the intermediate **485**. Since the reaction was conducted at elevated temperature, the isomerization of **485** to the observed product **480** was likely rapid in comparison to the rate at which **485** is being produced; as such, no **485** was ultimately detected in the product mixture.

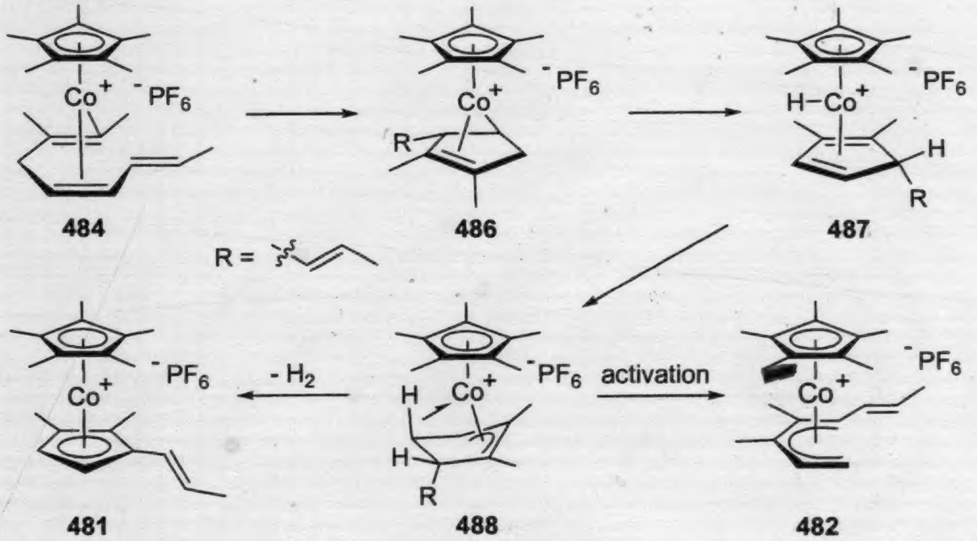
Scheme 4.35



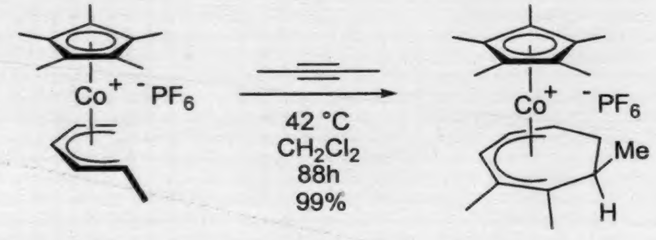
Since intermediate **484** bears a methyl group at the vinyl carbon, the metal center somewhat more sterically congested than the corresponding intermediate **461** formed from reaction of **430** with acetylene. As such, the required re-coordination of the pendant vinyl group of **484** should be slightly less favourable in comparison. For similar reasons, coordination of a second equivalent of 2-butyne would also be inhibited.

The formation of **481** and **482** might both arise from **484** as a result of a *five-membered* ring forming event (Scheme **4.36**). Upon this annulation and a subsequent β-hydride elimination/re-insertion sequence, vinyl olefin **484** would furnish the agostic allyl complex **488**. Spencer has previously demonstrated that such a complex would readily proceed directly to a pentadienyl complex (such as **482**) or to cyclopentadienyl complex (such as **481**) depending on the reaction temperature, and on the amount of adventitious water present.

Scheme 4.36


Co+
-PF6
484
Co+
-PF6
R
486
H-Co+
-PF6
H
R
487
R =
Co+
-PF6
- H2
481
H
Co+
-PF6
H
R
488
activation
Co+
-PF6
482

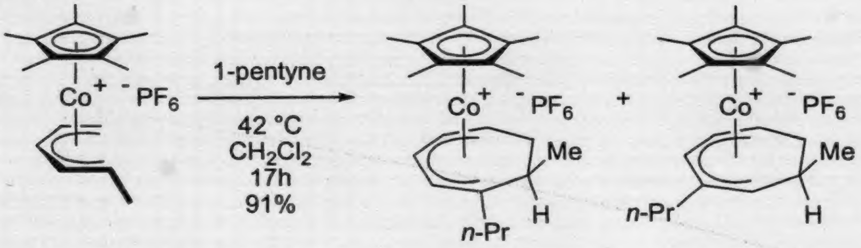
The by-products **481** and **482** could not be separated chromatographically from the major cycloheptadienyl product **480**. Fortunately, **480** was successfully prepared to the exclusion of these impurities by conducting the reaction at the intermediate temperature of 42 °C (Equation **4.32**). Although an extended reaction time was necessary to ensure complete reaction at this temperature, **480** was obtained in a quantitative yield and in a state of analytical purity by this method. Notably, the yield did not suffer from the use of dichloromethane directly from the bottle, without deoxygenation or drying.



430 **480** **(Eq. 4.32)**

In another trial, the same reaction was arrested after 19 hours and, upon removal of solvent and excess alkyne, an approximately 2:1 mixture of starting material and product **480** was obtained. In addition, however, a very small amount (less than 5% of the total) of a third product was visible to ^{1}H NMR spectroscopy. Although this minor component was not isolated from the mixture of **430** and **480**, it is tentatively identified as allyl olefin intermediate **485** by comparison to the ^{1}H NMR characteristics of the fully characterized complex **456**. Because the slightly elevated reaction temperature required for the formation of **485** from **430** was sufficient to promote the subsequent rearrangement of **485** to **480**, it seems unlikely that **485** could be obtained in good yield from this protocol.

1-Pentyne was assayed as a representative terminal alkyne, and was also incorporated into **430** in a [5+2] cycloaddition at 42 °C. As with 2-butyne, the reaction was very slow at room temperature and, under the slightly elevated temperature employed, no η^3,η^2-intermediate was recovered. Upon solvent removal and silica gel chromatography, a product mixture was isolated which was comprised of the regioisomers **489** and **490** in a 1:2 ratio (Equation **4.33**). The combined yield for the cycloaddition was 91%, and the products were characterized as a mixture as attempts to separate them by chromatography and crystallization failed.

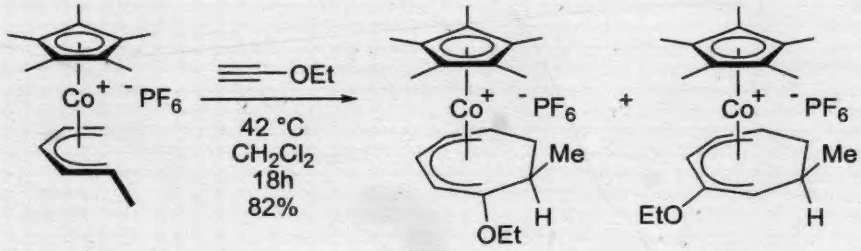


430 **489** **490**

1 : 2

(Eq. 4.33)

In an effort to investigate the factors influencing the regioselectivity (or lack thereof) of the [5+2] cycloaddition, ethoxyethyne was also assayed. This alkyne, although isosteric to 1-pentyne, is electronically activated at the terminus of the alkyne fragment owing to the electron-donating ethoxy group; despite this, the mixture of regioisomers isolated from an overnight reaction at 42 °C was almost identical in composition as that obtained from 1-pentyne (Equation **4.34**). At least on the basis of this result, the electronic nature of the alkyne has little influence on the regioselectivity of the migratory



430 **491** **492**

1 : 2

(Eq. 4.34)

insertion of this unit into the carbon-metal bond during the cycloaddition. Again, the regioisomers **491** and **492** could not be separated and were thus characterized as a mixture.

Several more sterically imposing monosubstituted alkynes were also assayed in an effort to determine the scope of the cycloaddition, as well as to investigate whether or not this steric bulk could be harnessed to improve the regioselectivity of the incorporation of terminal alkynes. Unfortunately, none of the bulky alkynes employed (*t*-butylacetylene, phenylacetylene, or trimethylsilylacetylene) yielded tractable seven-membered ring products upon treatment with **430**. In general, the bulky alkynes did not react with **430** at room temperature and, at slightly elevated temperature, afforded only a complicated mess with some paramagnetic components.

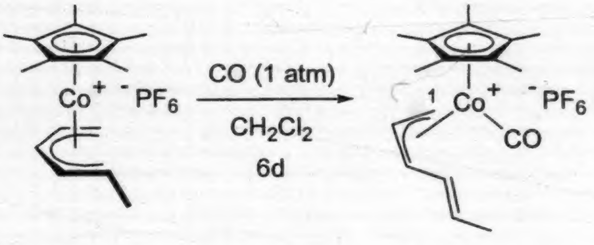
The electron deficient alkynes dimethyl acetylenedicarboxylate (DMAD) and methyl propionate were unreactive with **430** at room temperature as well as at 60 °C. On the other hand, the doubly propargylic dichloride 1,4-dichloro-2-butyne reacted with **430** at 30 °C overnight to furnish a paramagnetic blue-green solid that has not been identified; presumably an electron-transfer pathway generated a Co(II) product for which a blue-green colour is typical.

3. Reactions with non-alkyne ligands

The survey of ligands susceptible to insertion into Cp*Co(III) pentadienyl complexes was extended to several non-alkynes. No olefin has, to date, been successfully employed to date as competent substrates for the cobalt-mediated [3+2+2] cycloaddition.

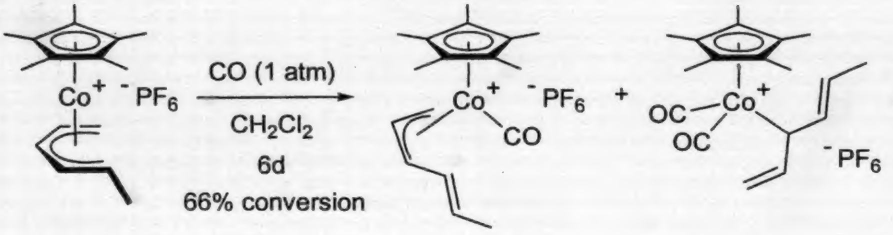
Likewise, attempts to induce a [5+2] cycloaddition of either ethylene or norbornylene with **430** yielded only unreacted starting materials.

On the other hand, storage of a dichloromethane solution of **430** at room temperature for 20 hours under an atmosphere of carbon monoxide resulted in approximately 25% conversion (by ^{1}H NMR integration) to the carbonylated Cp*Co(III) η^3-pentadienyl complex **493** (Equation **4.35**). The *anti,exo* structure of **493** is anticipated as the logical kinetic product from η^5-pentadienyl complex **430** upon decomplexation of the more substituted terminus of the pentadienyl ligand, and the magnitude of the measured vicinal coupling interaction ($^2J_{H2\text{-}H3}$ = 8.2 Hz) between the central allyl proton and the proton at the substituted allyl terminus confirms this geometry.



430 **493** **(Eq. 4.35)**

Upon standing for nearly a week, the ratio of product **493** to starting material **430** climbs to nearly 2:1. In addition, a third major component appears in the product mixture, which is tentatively assigned to the doubly-carbonylated Cp*Co(III) η^1-pentadienyl cation **494** (Equation **4.36**). It is a little surprising that the 3-η^1-pentadienyl complex is formed in favor of the conjugated primary 1-η^1-pentadienyl alternative, as the latter class of η^1-pentadienyls is generally more prevalent.[171] The formation of **494** is likely the result of a kinetic preference, not a thermodynamic one.



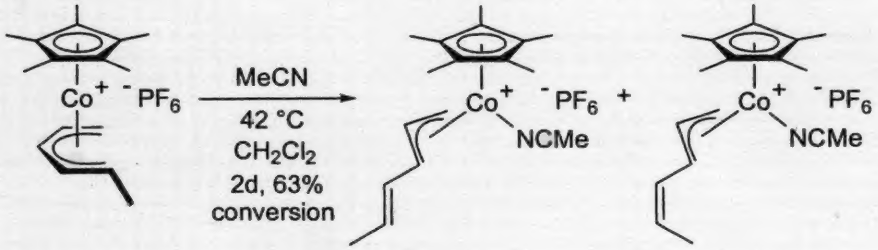
(Eq. 4.36)

430 **493** **494**

5 : 1

Unfortunately, all efforts to isolate and further characterize any carbonylated products from this reaction failed; only starting material **430** could be isolated from the mixture, indicating that the decarbonylation of **493** and **494** is very rapid. That **493** would decarbonylate rapidly was initially surprising, as Cp*Co(III) allyl carbonyl cations are well known to be resistant to decarbonylation under all but the most forcing conditions. However, Kirk has since demonstrated a similar observation amongst the CpCo(III) analogues: *anti* CpCo(III) η^3-pentadienyl carbonyl decarbonylates rapidly under ambient conditions whereas the corresponding *syn* isomer decarbonylates only upon heating. Presumably, the pendant vinyl group in η^3-pentadienyl complexes such as **493** is predisposed to promote decarbonylation only if placed in the *anti* stereochemistry.

A slightly different result was obtained when methylpentadienyl complex **430** was gently warmed in the presence of acetonitrile (Equation **4.37**). After 2 days, partial conversion to the η^3-pentadienyl acetonitrile adducts **495** and **496** was detected by NMR spectroscopy. Interestingly, the ^{1}H NMR data clearly supported the *syn* stereochemistry in both products, which differed from one another only in the stereochemistry about the pendant double bond; under the reaction conditions employed, the η^3-pentadienyl acetonitrile adducts are presumably able to isomerize to the presumably more thermodynamically stable *syn*, *exo* configuration. Once again, all efforts to isolate and characterize η^3-pentadienyl products by crystallization or chromatography from the reaction were frustrated as a result of the high lability of the acetonitrile ligand; in all cases, only starting material **430** could be recovered. Notably, no *endo* isomer of **430** was detected.

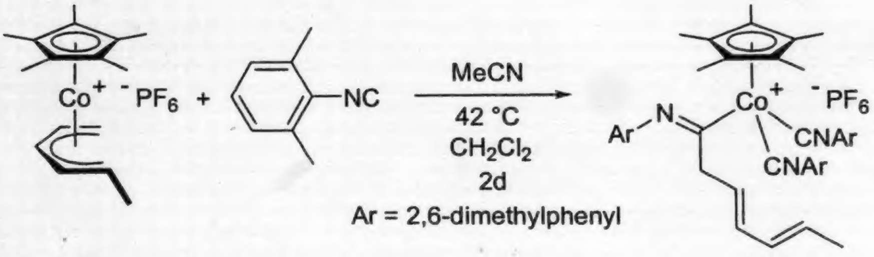


(Eq. 4.37)

430 **495** **496**

4 : 1

Upon heating η^5-methylpentadienyl complex **430** in the presence of 2,6-dimethylphenylisonitrile, a mixture of products is obtained in which the product **497** is the major (and only identifiable) component (Equation **4.38**). Although a migratory insertion of the isonitrile ligand into the metal-pentadienyl bond is clearly occurring, the insertion proceeds in a 1,1 fashion and is thus not likely to be productive in seven-membered ring formation. However, when taken with the results from the additions of carbon monoxide and acetonitrile described above, it is evident that dissociation in **430** from the η^5-pentadienyl to the η^3-pentadienyl binding mode proceeds at the substituted terminus of the pentadienyl ligand.


Co⁺ ⁻PF₆ +
NC
MeCN
42 °C
CH₂Cl₂
2d
Ar = 2,6-dimethylphenyl
Ar
N
Co⁺ ⁻PF₆
CNAr
CNAr

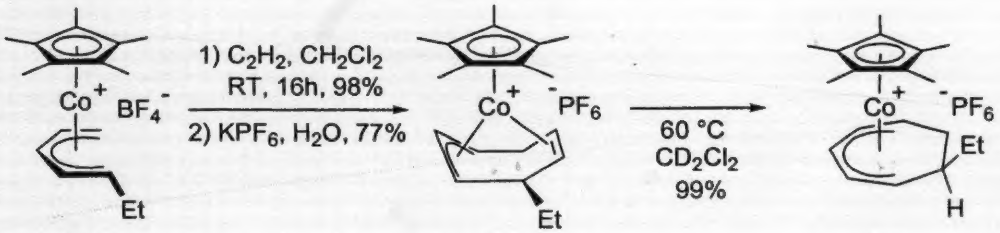
(Eq. 4.38)

430 **497**

*3. [5+2] Reactions of other Cp*Co(III) pentadienyl complexes*

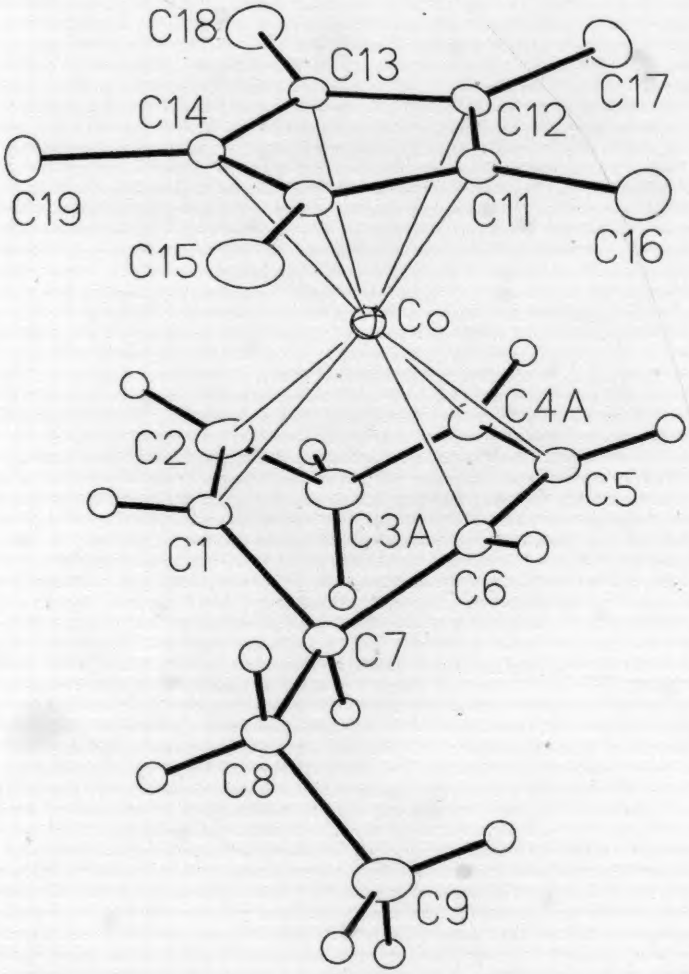
The Cp*Co(III) 1-ethylpentadienyl complex **359**, prepared and characterized previously by Spencer, reacted with acetylene in the same manner as the 1-methylpentadienyl complex **430** (Scheme **4.37**). X-Ray quality crystals of **498** were grown from a mixture of ether and dichloromethane. In all aspects, the [5+2] chemistry of **359** closely paralleled that of methyl-substituted homologue **430**.

Scheme 4.37


Co⁺ BF₄⁻
Et
1) C₂H₂, CH₂Cl₂
RT, 16h, 98%
2) KPF₆, H₂O, 77%
Co⁺ ⁻PF₆
Et
60 °C
CD₂Cl₂
99%
Co⁺ ⁻PF₆
Et
H

359 **498** **499**

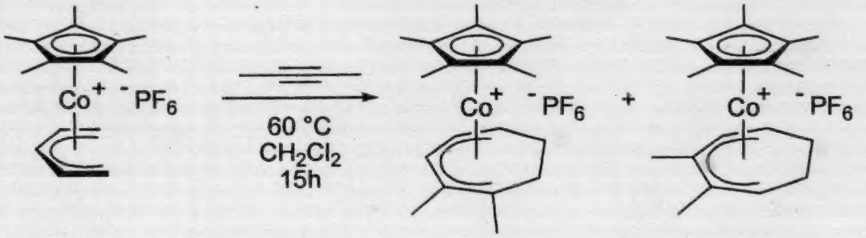
Figure 4.7: ORTEP for Complex **439** - University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0439


C18
C13
C17
C14
C12
C19
C11
C16
C15
Co
C4A
C2
C5
C3A
C1
C6
C7
C8
C9

Final Residuals: $R_1 = 0.0472$; $wR_2 = 0.1624$. Data collected at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): C1-C2, 1.374(3); C1-C7, 1.515(3); C2-C3A, 1.448(5); C3A-C4A, 1.480(6); C4A-C5, 1.517(5); C5-C6, 1.396(3); C6-C7, 1.513(3).

On the other hand, the parent pentadienyl complex **451** was unreactive towards a saturated solution of acetylene in dichloromethane. As well, heating a dichloromethane solution of **451** and 2-butyne overnight at 42 °C resulted only in the recovery of starting material. However, heating this same mixture overnight at 60 °C resulted in an almost complete consumption of starting material. The crude product mixture was very complicated and contained a number of unidentified compounds, as well as two compounds (**503** and **504**) which appeared to be the result of a successful [5+2] incorporation of alkyne (Equation **4.39**); **504** in particular had been previously prepared and characterized by Dzwiniel as a [3+2+2] cycloadduct. The yield of **503** and **504** is indeterminate as both compounds were part of a complicated mix of unknown compounds including a significant amount of unreacted starting material **451**.

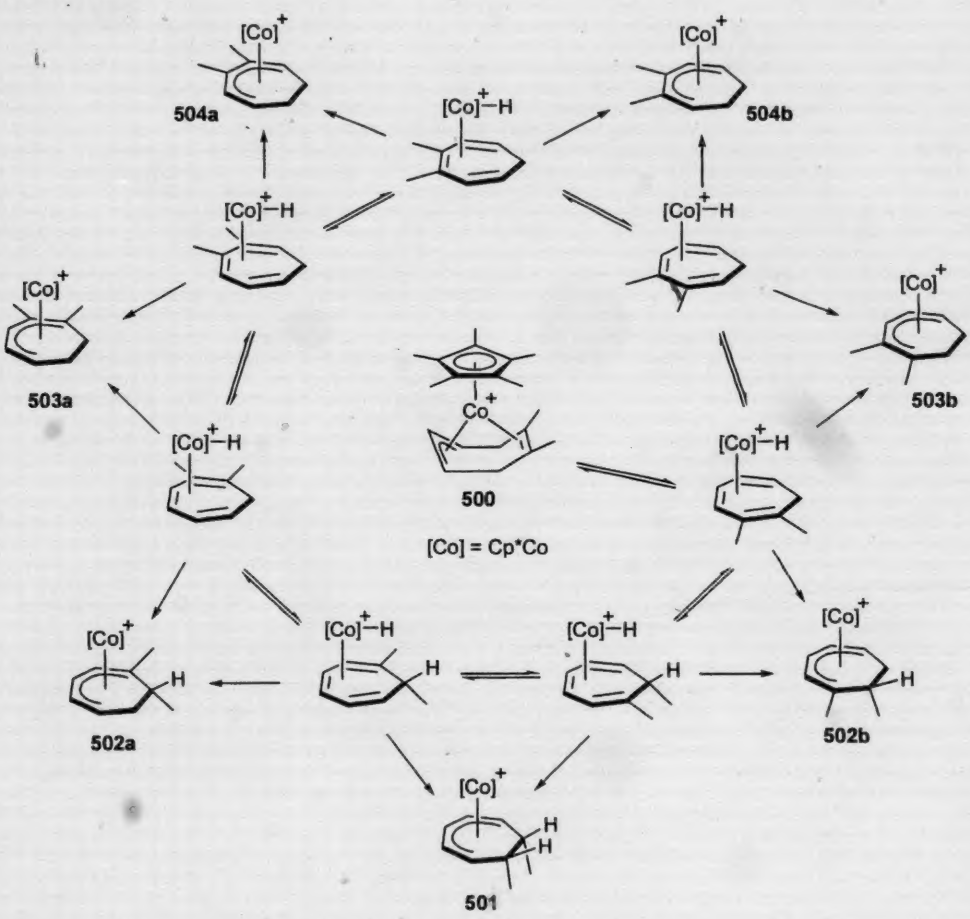


(Eq. 4.39)

451 **503** **504**

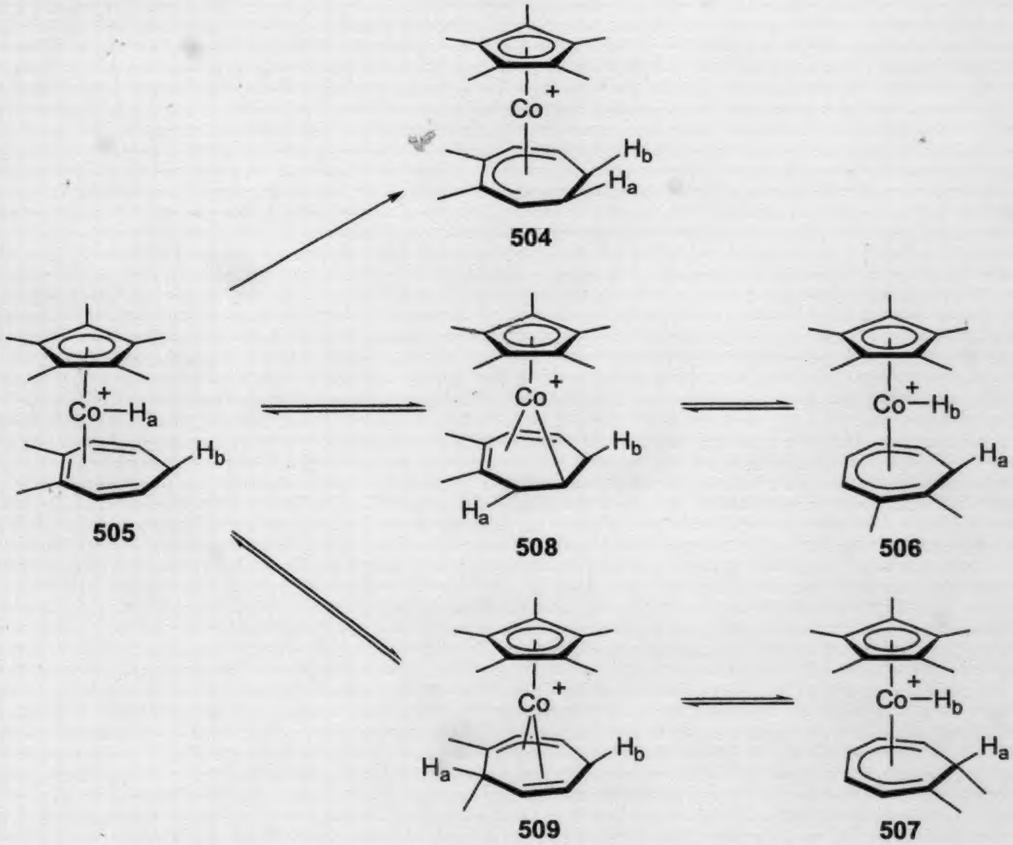
The presence of at least 2 different Cp*Co(III) cycloheptadienyl complexes in the product mixture highlights a potential selectivity issue in the [5+2] cycloaddition of pentadienyl complexes lacking an *anti* substituent at the pentadienyl terminus. Assuming that the expected *symmetric* η^3,η^2-allyl olefin intermediate **500** is formed, up to four structurally isomeric η^5-cycloheptadienyl products are accessible, of which three would exist as an enantiomeric pair. This relationship is summarized in Scheme **4.38**; the equilibrium arrows connecting the various triene hydride cations each represent several microscopic chemical steps. It must be noted that each triene hydride can exist as up to three related 18-electron η^4-isomers which can likely readily interconvert. For clarity, only one such isomer for each triene hydride is shown in Scheme **4.38** and in subsequent schemes.

Scheme 4.38


[Co]+
504a
[Co]+–H
[Co]+
504b
[Co]+–H
[Co]+–H
[Co]+
[Co]+
503a
503b
Co+
[Co]+–H
[Co]+–H
500
[Co] = Cp*Co
[Co]+
[Co]+–H
[Co]+–H
[Co]+
H
H
H
H
502a
502b
[Co]+
H
H
501

Etkin and Dzwiniel have previously elucidated the pathway by which σ-diene η^1,η^4-complexes formed as intermediates in [3+2+2] cycloaddition ultimately isomerize to the observed η^5 cycloheptadienyl products (Scheme **2.11**). Deuterium labelling studies have implicated the intermediacy of triene hydride cations similar to **505** (Scheme **4.39**) which isomerize via a rapid sequence of hydride insertions and eliminations. In the case of **505**, for example, an isomerization may proceed via several potential intermediates: the η^1,η^4-σ-diene complex **508**, the η^2,η^3- allyl olefin complex **509**, or the η^5-

Scheme 4.39



cycloheptadienyl complex **504**. These three complexes represent the immediate products of the hydride migration of the triene hydride **505**, in which the hydride could, in principle, be placed at any of the 6 carbons bonded to the metal.

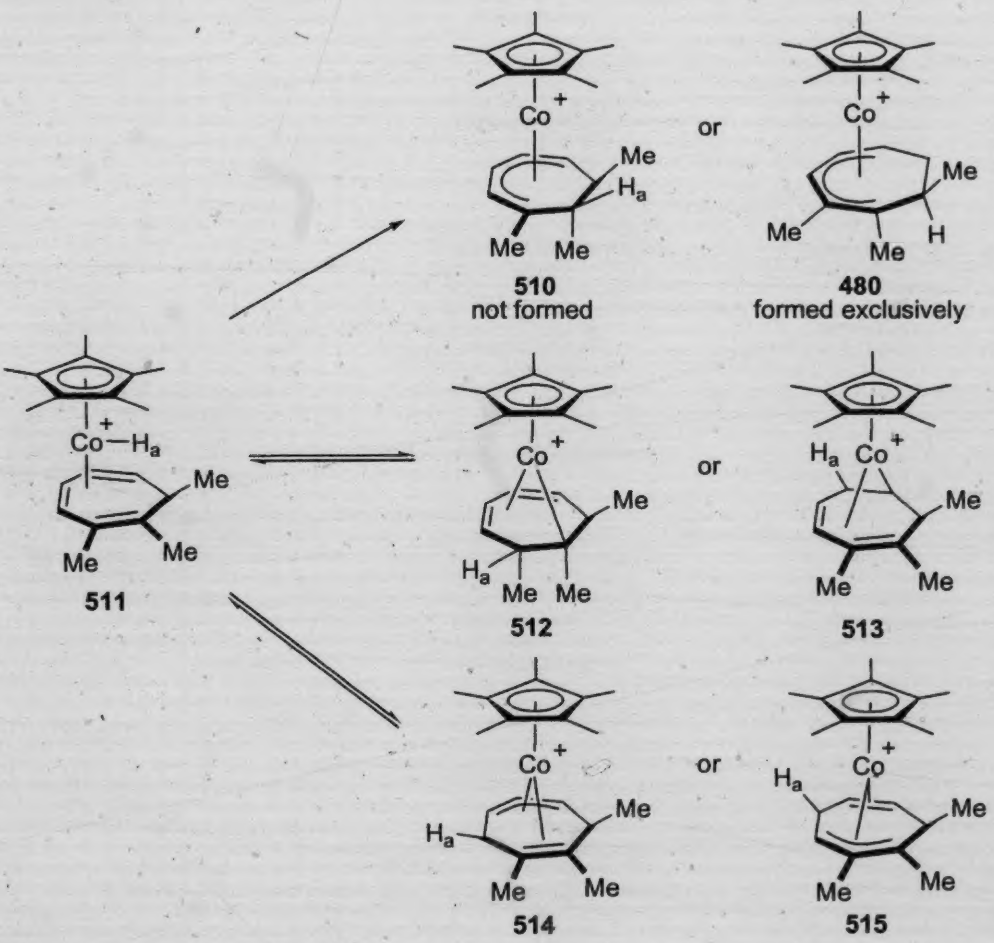
Etkin and Dzwiniel have shown that the activation of the saturated carbon-hydrogen bond of Cp*Co(III) η^5-cycloheptadienyl [3+2+2] cycloadducts such as **504** does not occur under the reaction conditions employed. The hydride migration to form these complexes is therefore not reversible and as a result, complexes such as **504** are not productive intermediates for the interconversion of triene hydride cations. Once a hydride migrates to a terminus (C1 or C6) of the triene fragment, it no longer re-activates.

Migration in **505** to C3 or C4 would generate η^3,η^2-cycloheptadienyl complexes akin to **509**. As stated earlier in this thesis (Chapter 2), these intermediates cannot be categorically dismissed as active on the hydride isomerization manifold, but it is noteworthy that no such intermediate has even been isolated from a [3+2+2] reaction even though these compounds (as shown in this chapter) are stable under normal [3+2+2] reaction conditions.

On the other hand, Etkin and Dzwiniel have also demonstrated that the migration to C2 or C5 of the triene fragment is reversible, and occurs at a much faster rate than the irreversible migration to a terminus. As such, there is opportunity for rapid interconversion between any number of triene hydride complexes before a final migration which yields an isolated Cp*Co(III) η^5-cycloheptadienyl product.

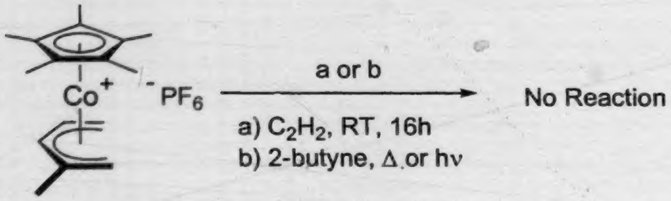
This is all in stark contrast to the reaction described earlier in this chapter of 2-butyne with **430** (Equation **4.32**), which could *potentially* yield only 2 possible Cp*Co(III) cycloheptadienyl products (Scheme **4.40**): **480** and **504**, of which only **480** was actually produced. Because the intermediates **512** – **515** each possess only one activatable *endo* hydrogen (H_a), there is only one accessible triene hydide (**511**) on the entire manifold which can exist as any one of three possible η^4-isomers. If any of **513** –

Scheme 4.40


Co+
Me
Ha
Me Me
510
not formed
or
Co+
Me
Me
Me
H
480
formed exclusively
Co+—Ha
Me
Me
Me
511
Co+
Me
Ha
Me Me
512
or
Ha Co+
Me
Me
Me
513
Co+
Me
Ha
Me
Me
514
or
Ha
Co+
Me
Me
Me
515

516 form during the rapid hydride migration sequence, the formation is ultimately reversed. Only migration to a terminal carbon of **511** is irreversible and therefore only cycloheptadienyl complexes may ultimately emerge from this manifold. Although either **480** or **510** could result, the migration to form **480** must be *kinetically* favored over the formation of **510**. Although the reason for this kinetic selectivity is not completely understood, the explanation likely lies in the fact that only one terminus of the triene hydride **511** bears a substituent. As such, the carbon-metal bond to this terminus will likely be longer than the corresponding bond at the other terminus and as such, less accessible for a subsequent migratory insertion.

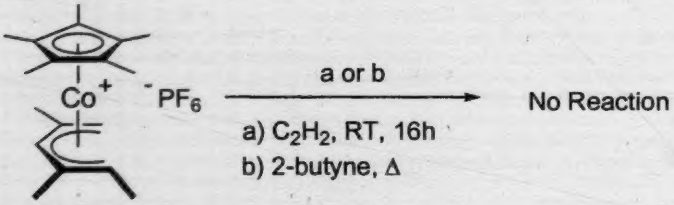
It is therefore evident that a substituent at the terminus of an η^5-pentadienyl ligand complexed to a Cp*Co(III) template confers enhanced reactivity with respect to [5+2] cycloaddition, as well as enhanced regioselectivity in product formation. Complex **452** was next assayed to investigate the effect of a substituent at C2 of the pentadienyl fragment. Unfortunately, all efforts to induce a [5+2] cycloaddition of the 2-methylpentadienyl complex **452** met only with frustration. No reaction occurred with acetylene as a saturated dichloromethane solution at room temperature, or with 2-butyne at 42 °C. A cycloaddition attempt at 60 °C with 2-butyne also furnished only starting material overnight although in this case, significant broadening of the ^{1}H NMR spectrum indicated some decomposition along a paramagnetic pathway. As well, insoluble red-orange material was evident; none of the expected or desired intermediates or products should be insoluble in dichloromethane. Attempts to induce the cycloaddition photolytically also failed; irradiation of a dichloromethane solution of **452** and 2-butyne returned only starting material (Equation **4.40**).



452

(Eq. 4.40)

Equally unreactive in these trial reactions was the 1,2,4-tri-substituted pentadienyl complex **454**, although fewer attempts were made with this substrate owing to the smaller quantity available. Again, no reaction was observed with a saturated solution of acetylene in dichloromethane, nor with 2-butyne at room temperature or at slightly elevated temperatures (Equation **4.41**).

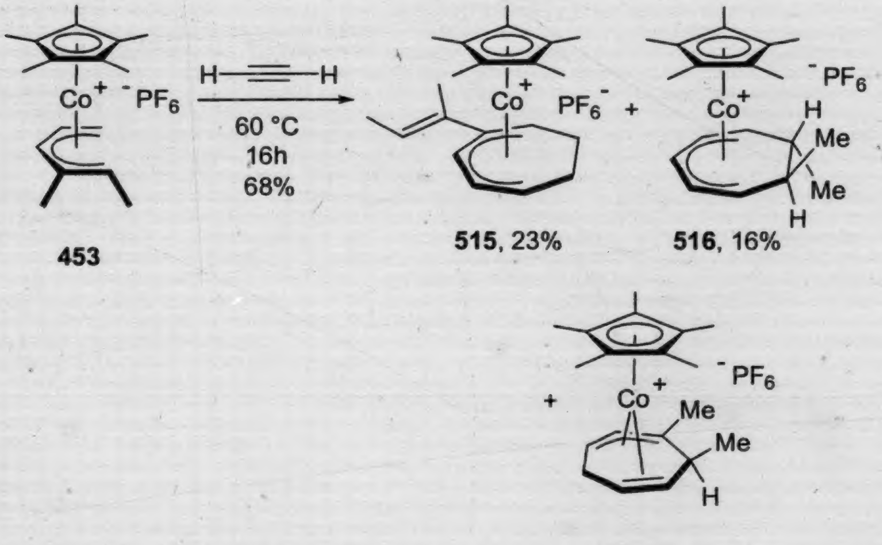


454

(Eq. 4.41)

On the other hand, preliminary trials employing the di-substituted complex **453** have proven more fruitful, although these assays have so far included very small scale probe reactions owing to the small amount of **453** originally made. In general, this complex appears more reactive towards alkynes than parent pentadienyl complex **451**, 2-methyl analogue **452**, and the trisubstitued analogue **454**, but less reactive than the terminally substituted pentadienyl complexes **430** and **359**.

Although no reaction is observed when dimethylpentadienyl complex **453** is stored overnight at room temperature in a dichloromethane solution saturated with acetylene, when the same mixture is heated at 60 °C overnight in a glass bomb, **453** is completely converted into a mixture of three compounds which are tentatively assigned on the basis of ^{1}H and COSY NMR (Equation **4.42**). Surprisingly, the major species present in the mixture is the η^3,η^2-cycloheptadienyl complex **517**; it is remarkable that **517** resists conversion to the conjugated isomer **516**, as **516** constitutes a relatively minor component in the mixture even after heating at 60 °C. The remaining species is tentatively assigned as Cp*Co η^5-cycloheptadienyl species **515**, which is analogous to **469** formed as a byproduct in the related reaction between 1-methylpentadienyl complex **430** and acetylene (Equation **4.26**).



(Eq. 4.42)

453

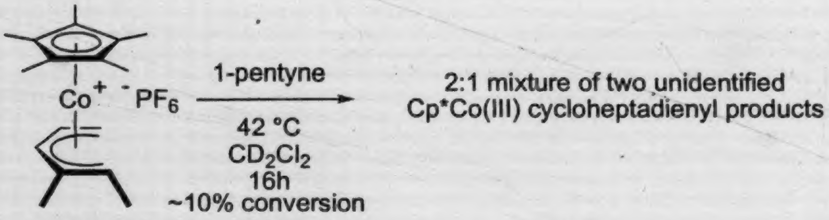
515, 23%

516, 16%

517, 61%

Three NMR-tube reactions were performed to assay the reactivity of 1,2-dimethylpentadienyl complex **453** with substituted alkynes. A solution of **453** with each of 2-butyne, 1-pentyne, and ethoxyacetylene was prepared in CD_2Cl_2 and heated at 42 °C. Even after 4 days, 2-butyne showed no reactivity under these conditions with the pentadienyl complex.

On the other hand, the monosubstituted alkynes yielded promising, albeit complicated results. After 16 hours at 42 °C, NMR interrogation of the reaction between 1-pentyne and **453** (Equation **4.43**) revealed the consumption of approximately 10 percent of the pentadienyl starting material in favor of at least two compounds that may tentatively be assigned as Cp*Co(III) cycloheptadienyl complexes on the basis of ^{1}H NMR spectroscopy.

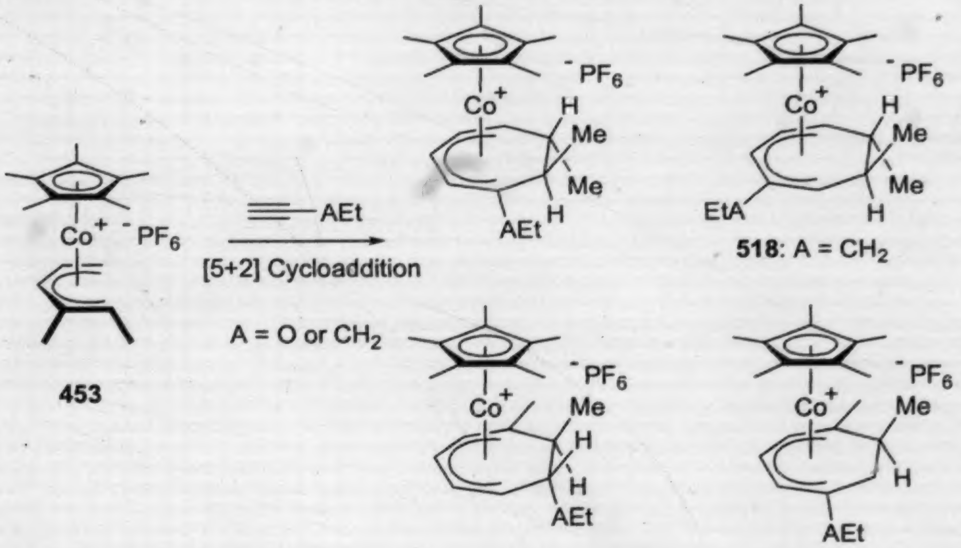

Co⁺ ⁻PF₆
1-pentyne
42 °C
CD₂Cl₂
16h
~10% conversion
2:1 mixture of two unidentified
Cp*Co(III) cycloheptadienyl products

453

(Eq. 4.43)

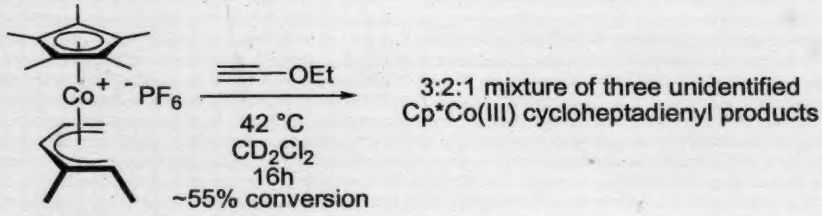
The exact structure of the products rem to be unambiguously determined as at least four cycloheptadienyl complexes might be accessed by a [5+2] cycloaddition and the majority of the ^{1}H NMR signals are obscured by partial or complete overlap with other signals present (Figure **4.8**). Based on the emergence of a doublet ($J = 7.0$ Hz) at 6.27 ppm, however, the major cycloheptadienyl product can be *tentatively* assigned as

Figure 4.8: Four Possible [5+2] Cycloadducts from Complex **453**


Co+
-PF6
453
AEt
[5+2] Cycloaddition
A = O or CH2
Co+
-PF6
H
Me
Me
H
AEt
EtA
518: A = CH2
Me
H
H
AEt

518 as this is the only expected product that would not exhibit a triplet at this chemical shift.

The parallel reaction with ethoxyacetylene (Equation **4.44**) proceeded more rapidly as, after 16 hours at 42 °C, approximately 55% of the dimethylpentadienyl complex **453** was converted into an approximately 3:2:1 mixture of three cycloheptadienyl products although, again, these products remain to be unambiguously identified. Further investigation of the [5+2] cycloaddition chemistry of 1,2-dimethylpentadienyl complex **453** is being conducted presently in the Stryker group.


Co
+
-
PF6
OEt
42 °C
CD2Cl2
16h
~55% conversion
3:2:1 mixture of three unidentified
Cp*Co(III) cycloheptadienyl products

453

(Eq. 4.44)

Part F: Summary and Future Work

Based on the investigations conducted to this date, a discussion of the known and postulated aspects of the [5+2] cycloaddition can be conducted. Apart from the reaction conditions employed (temperature, solvent, reaction time), the factors which influence the outcome of an attempted [5+2] cycloaddition can be effectively broken into three categories: the role and nature of the pentadienyl ligand, the role and nature of the alkyne, and the role and nature of the metal template (as well as any spectator ligands).

A small number of pentadienyl ligands have been employed to date in this study. In general, those bearing a single substituent at the terminus of the pentadienyl fragment (**430** and **453**) have been by far the most productive in [5+2] cycloaddition chemistry.

A single substituent in the 2-position of the pentadienyl fragment appears, at least in initial trials, to actually inhibit the [5+2] cycloaddition: the 2-methylpentadienyl complex **452** remained unreactive towards 2-butyne under conditions which effected a cycloaddition, albeit messy, of the unsubstituted complex **451**.

The nature of the alkyne is also of some consequence. In reactions with 1-methylpentadienyl substrate **430**, both steric and electronic aspects of the alkynes had a role to play in the observed [5+2] reactivity (or lack thereof).

The electron-deficient alkynes DMAD and methyl propionate were non-productive in attempted [5+2] cycloadditions with **430**. Furthermore, the preliminary NMR-tube investigation of the reactivity of 1,2-dimethylpentadienyl complex **453** revealed that increased electron richness at the alkyne accelerates the rate of [5+2] cycloaddition. As ethoxyethyne is isosteric with 1-pentyne, the greater rate of [5+2] cycloaddition in this case is almost certainly due to the increased electron-richness of this propargyl ether. This is consistent with the lack of reactivity of the electron deficient alkynes that had also been employed.

The lack of reactivity of 2-butyne with the 1,2-dimethylpentadienyl complex **453**, on the other hand, reveals a steric influence on the rate of reaction. As a disubstituted alkyne, 2-butyne is more electron rich than the monosubstitued 1-pentyne. However, the terminal alkyne (1-pentyne) is clearly reacting more slowly than the internal one; presumably substituents at either end of the alkyne play a steric role in inhibiting [5+2] reactivity. It is not entirely clear whether this steric imperative impedes inital alkyne coordination, or whether it is the subsequent carbon-carbon bond-forming insertion step which is retarded by the steric bulk. This steric influence may also be responsible for the inability of **149** to incorporate the bulky alkynes *t*-butylacetylene and phenylacetylene.

In the case of electron deficient alkynes such as methyl propynoate, which do not undergo [5+2] cycloaddition with **453**, it may be that the electron-poorness of the alkyne inhibits coordination to the metal. Since the alkyne would need to be coordinated by a 16-

electron cationic Co(III) template, it may be that the alkyne needs to be a significant σ-donor in order for any significant amount of coordination to occur. It must be borne in mind, however, that the formation (albeit temporarily) of the carbonylated Cp*Co(III) η^3-pentadienyl cations **493** and **494** and the related acetonitrile adducts **495** and **496** demonstrates that the cationic 16-electron Cp*Co(III) *is quite capable* of binding ligands which are poor σ-donors, but strong π-acceptors. It is therefore also quite probable that the [5+2] cycloaddition of electron-poor alkynes is inhibited at the initial bond-forming step.

The other substrate factor at play in these [5+2] cycloadditions is the role of the Cp*Co template. This template was first employed for no other reason that the initial availability of the Cp*Co(III) 1-methylpentadienyl substrate from a tangentially related [3+2+2] study. As such, there is no reason to assume that the [5+2] reactivity is limited to this template.

The related unsubstituted (and more electron deficient) CpCo(III) template is currently under investigation in the Stryker group for its applicability to the [5+2] cycloaddition. Kirk[277,278] has, in fact, successfully induced the [5+2] cycloaddition of the parent CpCo(III) pentadienyl complex with 2-butyne under milder conditions than those necessary for the messy reaction of **451** with 2-butyne. Apart from potentially offering a broader scope in [5+2] chemistry, a CpCo template is preferable to the Cp*Co alternative because of the increased time and expense associated with the preparation of Cp*. From the point of view of atom economy, CpCo is also one of the most attractive sources of 6 ligand electrons.

To better understand these mechanistic issues and to broaden the scope of this novel [5+2] cycloaddition, there is much potential for future work. As indicated, the parent CpCo(III) template is currently under investigation, but there is a broad realm of alternative templates that must be considered, including those based on non-Cp ligands such as Tp, and those based on metals other than cobalt. Alkyne chemistry beyond the first row of the transition series often differs appreciably from that of the first row, especially where terminal alkynes are employed, and it is not known whether rhodium or iridium will mediate an analogous cycloaddition. As well, plans are being made to investigate the [5+2] cycloaddition as templated by the neutral iron analogues.

Chapter 2 of this thesis described the formation of bicyclic organic compounds containing seven-membered rings installed via the more established [3+2+2] cycloaddition. One of the major limitations of the [3+2+2] cycloaddition for this chemistry is that the Cp*Co(III) cycloheptadienyl products are formed in sometimes modest yield, and are often contaminated with significant levels of impurity that cannot be readily removed. The [5+2] cycloaddition represents an exciting complementary alternative to the [3+2+2] reaction for the synthesis of Cp*Co η^5-cycloheptadienyl complexes, and is currently being investigated by Ylijoki[279] in the Stryker group to this end. Ylijoki has already realized the formation of Cp*Co(III) η^5-cycloheptadienyl complexes bearing pendant nucleophiles via [5+2] cycloaddition with yields and product purities superior to those furnished by the [3+2+2] cycloaddition.

As well, the chemistry of the Cp*Co(III) η^3,η^2-cycloheptadienyl complexes themselves warrants further investigation, as this binding mode was heretofore unknown in seven-membered rings. Although many of the η^3,η^2-cycloheptadienyl complexes prepared as part of the present investigation may be prone to isomerization to the more familiar η^5-binding mode, the surprising stability of complex **517**, for example, reveals that the η^3,η^2-cycloheptadienyl hapticity may be much more robust than previously imagined. Complexes of this sort must be investigated as electrophiles for the formation of 1,4-cycloheptadiene ligands akin to those formed kinetically by central-carbon addition to conjugated η^5-cycloheptadienyl complexes as described in Chapter 2.

Chapter 5 – Experimental

Part A: General Experimental

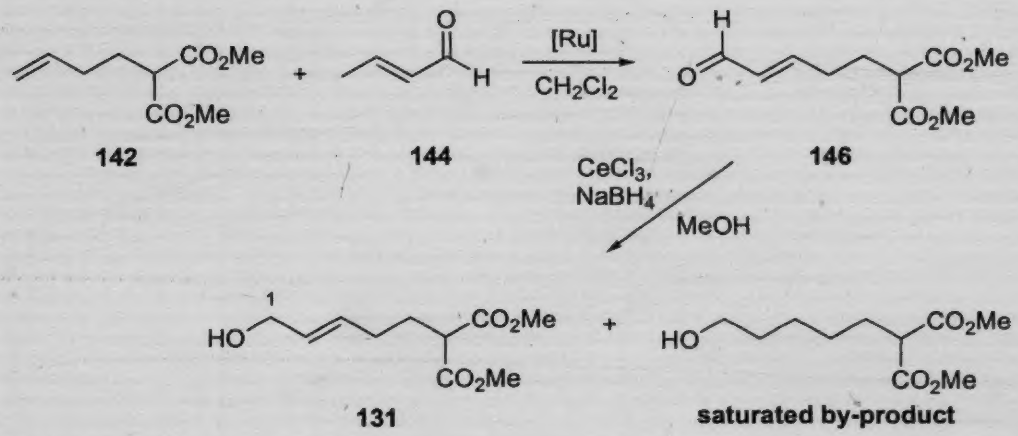
Reagents and Methods: All manipulations of air sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques, or under a nitrogen atmosphere in a Vacuum Atmospheres He-553-2 Dri-lab equipped with a Mo-41-1 inert gas purifier and a CD-882 Dri-Cold Freezer maintained at -35 °C, or an MBraun Labmaster 100 equipped with a -35 °C freezer. Toluene, benzene, tetrahydrofuran, diethyl ether, hexane and pentane were distilled under a nitrogen atmosphere either from sodium (toluene), sodium benzophenone ketyl (tetrahydrofuran, diethyl ether, and benzene) or potassium benzophenone ketyl (pentane and hexane). Reagent grade acetone was vacuum-transferred from boric acid anhydride and stored in the glove box with no further purification. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed as necessary by a stream of inert gas, or by repeated freeze-pump-thaw cycles. Unless stated otherwise, all reactions were carried out under an inert atmosphere. Photolysis was carried out using a Hanovia 450 watt high pressure mercury lamp filtered through pyrex.

In the case of some cationic Co(III) complexes, very slow crystallization was accomplished by making use of a method described herein as "pinhole diffusion". In this method, a small amount (usually less than 25 mg) of the sample was dissolved in a single solvent (usually dichloromethane) within a small glass tube (6 mm i.d., 50 mm length). The tube was completely filled with additional solvent, and sealed with an NMR-tube cap which had been perforated once with a narrow-gauge needle. This tube was then carefully placed into a large sample vial which was, in turn, filled with a second solvent (usually diethyl ether) in which the complex had virtually no solubility. Diffusion between the two solvents via the pinhole was extremely slow and, as a result, it often took several weeks for complete crystal growth.

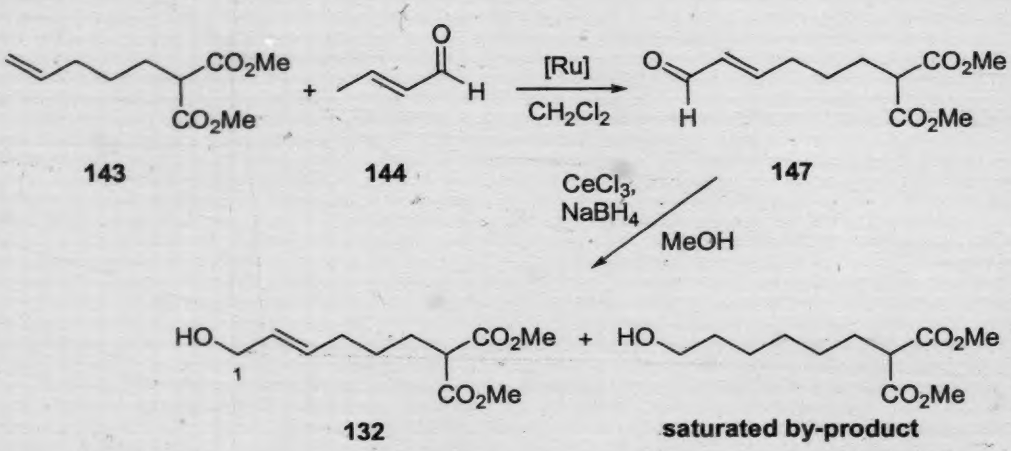
Instrumentation: IR spectra were recorded on a Nicolet Magna IR 750 spectrophotometer equipped with a Nic-Plan FTIR Microscope. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer, a Varian Inova 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer, a Varian Inova 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer, a Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or a Varian Unity-Inova 300 (^{1}H, 300 MHz) spectrometer. ^{1}H NMR chemical shifts are reported in ppm relative to external TMS using residual protiated solvent resonances as internal reference. ^{13}C NMR chemical shifts are similarly referenced against external TMS using deuterated solvent signals. Routine low- and high-resolution electron impact mass spectra were obtained on a Kratos MS-50 spectrometer with an ionization energy of 70eV. Electrospray mass spectra were obtained on a Micromass ZabSpec oaTOF spectrometer or an Agilent Technologies 1100MSD spectrometer. Elemental analyses were performed by the University of Alberta Microanalysis Laboratories, utilizing a Carlos Erba Instruments CHSN-O EA1108 Elemental Analyzer. X-Ray structural data was collected on a Bruker PLATFORM diffractometer with a SMART 1000 CCD area detector. All data collection was performed at -80 °C. All data collection, structural solutions, and further refinements were performed by Dr. Robert McDonald and Dr. Michael J. Ferguson of the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. The positions of hydrogen atoms shown in ORTEP diagrams in this dissertation are, in all cases, estimated.

Further Note on Spectroscopic Methods. In ^{1}H NMR spectral data, values of the coupling constants are obtained directly from the spectrum. Although generally measured to ± 0.1 Hz, *J* values are self-consistent only to ~ ± 0.5 Hz. GCOSY denotes the standard COSY experiment, aquired using field gradients. Data for the ^{1}H-^{1}H COSY or GCOSY is presented such that correlations are listed only once. ^{1}H-^{13}C HETCORR experiments are recorded at the ^{13}C frequency of the spectrometer, while HMQC and HMBC are recorded at the ^{1}H frequency.

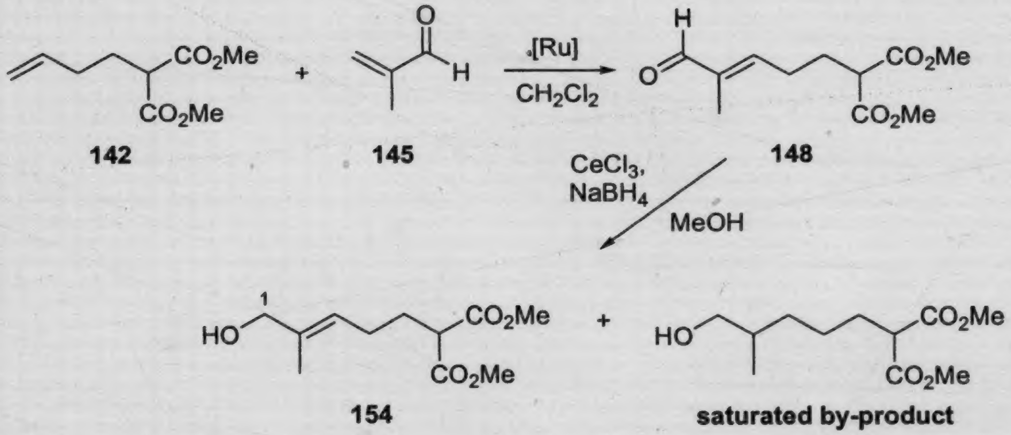
Starting Materials. All commercial materials were purified prior to use by distillation or crystallization as appropriate. The following compounds were prepared and purified according to literature methods: $Cp^{*}Co(C_2H_4)_2$ **43**,[280-282] Cp*Co bis(vinyltrimethylsilane) **160**,[126-128] dimethyl allylmalonate,[123] dimethyl 3-butenylmalonate,[123] dimethyl 4-pentenylmalonate,[124] Cp*Co(III) cycloheptadienyl hexafluorophosphate **473**.[17]


CO2Me
CO2Me
142
+
O
H
144
[Ru]
CH2Cl2
H
O
CO2Me
CO2Me
146
CeCl3,
NaBH4
MeOH
1
HO
CO2Me
CO2Me
131
+
HO
CO2Me
CO2Me
saturated by-product

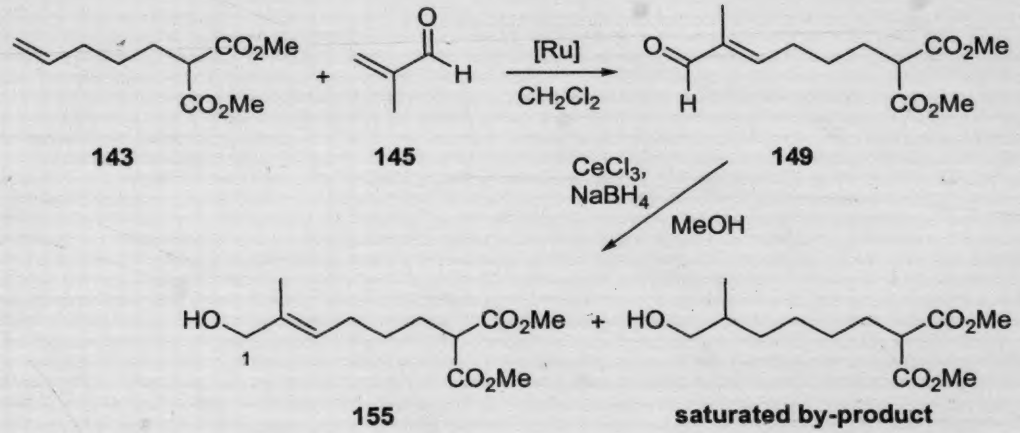
Dimethyl 5-hydroxy-3-pentenylmalonate (131): A round-bottom flask was charged with a solution of dimethyl 3-butenylmalonate **142** (2.47 g, 13.3 mmol), crotonaldehyde (2.50 mL, 30.2 mmol), and 2nd generation Grubbs catalyst (565.1 mg, 0.666 mmol, 5 mol %) in freshly distilled dichloromethane (50 mL). The faintly orange mixture was maintained at reflux for 3 hours under a very gentle stream of argon. After cooling, the solvent was removed *in vacuo* and replaced with methanol (~ 40 mL). The solution was cooled to -78 °C, and $CeCl_3 \cdot 7H_2O$ (5.45 g, 14.6 mmol) was added with rapid stirring. Over the course of 30 minutes, $NaBH_4$ (0.5551g, 14.7 mmol) was carefully added in small portions to the rapidly-stirring solution while the temperature was maintained at -78 °C. During this time, a clumpy white precipitate began to form. Once addition was complete, the reaction was allowed to warm to room temperature, and stirring continued for an additional 30 minutes. The reaction mixture was then poured into saturated aqueous ammonium chloride (~ 100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over solid $CaCl_2$, filtered, and finally concentrated *in vacuo* to furnish crude **131** as a pale yellow oil. Silica gel chromatography with diethyl ether as eluent afforded **131** (1.75 g, 8.09 mmol, 61%) as a yellow oil. A small amount (~9%) of saturated analogue was present as an impurity in **131** as determined by ^1H NMR integration of the triplet at 3.65 ppm but **131** was otherwise free of impurity. IR (neat film, cm^{-1}) 3419 (m, br), 3004 (w), 2955 (m), 2862 (m), 1737 (s), 1438 (s), 1345 (m), 1249 (s), 1157 (s), 1085 (w), 1013 (m), 972 (m), 901 (w), 804 (w), 697 (w); ^1H NMR (500 MHz, $CDCl_3$) δ 5.66 (m, 2H, H_2 and H_3), 4.09 (d, 2H, $J_{H1\text{-}H2} = 4.4$ Hz, H_1), 3.74 (s, 6H,-$OC\underline{H}_3$), 3.38 (t, 1H, $J_{H5\text{-}H6} = 7.4$ Hz, H_6), 2.10 (m, 2H, H_4), 2.01 (m, 2H, $J_{H5\text{-}H6} = 7.4$ Hz, H_5), 1.38 (broad s, 1H, -$O\underline{H}$); ^1H-^1H GCOSY (500 MHz, $CDCl_3$) δ 5.66 ↔ δ 4.09, δ 2.10; δ 4.09 ↔ δ 2.10; δ 3.38 ↔ δ 2.01; δ 2.10 ↔ δ 2.01; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (-$\underline{C}O_2CH_3$), 130.7 (two resonances ~0.02 ppm apart, C_2 and C_3), 63.5 (C_1), 52.5 (-$CO_2\underline{C}H_3$), 50.9 (C_6), 29.8 (C_4), 28.1(C_5); HMQC (500 MHz, $CDCl_3$) δ 130.7 ↔ δ 5.66; δ 63.5 ↔ δ 4.09; δ 52.5 ↔ δ 3.74; δ 50.9 ↔ δ 3.38; δ 29.8 ↔ δ 2.10; δ 28.1 ↔ δ 2.01. Analysis calculated for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46; found: C, 55.31; H, 7.59.



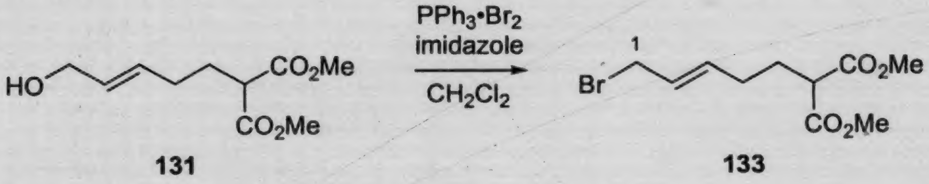
Dimethyl 6-hydroxy-4-hexenylmalonate (132): A round-bottom flask was charged with a solution of dimethyl 4-pentenylmalonate **143** (2.55 g, 12.7 mmol), crotonaldehyde (2.50 mL, 30.2 mmol), and 2nd generation Grubbs catalyst (582.1 mg, 0.686 mmol, 5 mol %) in freshly distilled dichloromethane (50 mL). The faintly orange mixture was maintained at reflux for 3 hours under a very gentle stream of argon. After cooling, the solvent was removed *in vacuo* and replaced with methanol (~ 40 mL). The solution was cooled to -78 °C, and $CeCl_3 \cdot 7H_2O$ (5.50 g, 14.8 mmol) was added with rapid stirring. Over the course of 30 minutes, $NaBH_4$ (0.5656 g, 15.0 mmol) was carefully added in small portions to the rapidly-stirring solution while the temperature was maintained at -78 °C. During this time, a clumpy white precipitate began to form. Once addition was complete, the reaction was allowed to warm to room temperature, and stirring continued for an additional 30 minutes. The reaction mixture was then poured into saturated aqueous ammonium chloride (~ 100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over solid $CaCl_2$, filtered, and finally concentrated *in vacuo* to furnish crude **132** as a pale yellow oil. Silica gel chromatography of **132** with diethyl ether as eluent afforded **132** as a yellow oil (1.62 g, 6.90 mmol, 54%). A small amount (~10 %) of saturated analogue was present as an impurity in **132** as determined by ^{1}H NMR integration of the triplet at 3.62 ppm but **132** was otherwise free of impurity. IR (neat film, cm^{-1}) 3407 (m, br), 3002 (w), 2955 (m), 2863 (m), 1736 (s), 1437 (s), 1346 (m), 1219 (m), 1154 (m), 1114 (w), 1089 (w), 1055 (w), 1004 (w), 972 (w), 905 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (m, 2H, H_2 and H_3), 4.08 (m, 2H, H_1), 3.73 (s, 6H,-$OC\underline{H}_3$), 3.36 (t, 1H, $J_{H6\text{-}H7}$ = 7.5 Hz, H_7), 2.08 (m, 2H, H_4), 1.91 (m, 2H, H_6), 1.45 (broad s, 1H, -$O\underline{H}$), 1.41(m, 2H, H_5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (-$\underline{C}O_2CH_3$), 132.0 (C_2 or C_3),129.8 (C_2 or C_3), 63.6 (C_1), 52.5 (-$CO_2\underline{C}H_3$), 51.5 (C_7), 31.7 (C_4), 28.3 (C_6), 26.7(C_5); HMQC (500 MHz, $CDCl_3$) δ 132.0 ↔ δ 5.65; δ 129.8 ↔ δ 5.65; δ 63.5 ↔ δ 4.08; δ 52.5 ↔ δ 3.73; δ 51.5 ↔ δ 3.36; δ 31.7 ↔ δ 2.08; δ 28.3 ↔ δ 1.92; δ 26.7 ↔ δ 1.41. Analysis calculated for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; found: C, 57.30; H, 7.99.



Dimethyl 5-hydroxy-4-methyl-3-pentenylmalonate (154): A round-bottom flask was charged with a solution of dimethyl 3-butenylmalonate **142** (2.58 g, 13.9 mmol), methacrolein (2.50 mL, 30.2 mmol), and 2nd generation Grubbs catalyst (549.6 mg, 0.647 mmol, 5 mol %) in freshly distilled dichloromethane (50 mL). The faintly orange mixture was maintained at reflux for 3 hours under a very gentle stream of argon. After cooling, the solvent was removed *in vacuo* and replaced with methanol (~ 40 mL). The solution was cooled to -78 °C, and $CeCl_3 \cdot 7H_2O$ (5.58 g, 15.0 mmol) was added with rapid stirring. Over the course of 30 minutes, $NaBH_4$ (562.1 mg, 14.9 mmol) was carefully added in small portions to the rapidly-stirring solution while the temperature was maintained at -78 °C. During this time, a clumpy white precipitate began to form. Once addition was complete, the reaction was allowed to warm to room temperature, and stirring was continued for an additional 30 minutes. The reaction mixture was then poured into saturated aqueous ammonium chloride (~ 100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over solid $CaCl_2$, filtered, and finally concentrated *in vacuo* to furnish crude **154** as a pale yellow oil. Silica gel chromatography of **154** with diethyl ether as eluent afforded **154** (1.70 g, 7.4 mmol, 53%) as a yellow oil. A small amount (~ 3%) of saturated by-product was present as an impurity in **154** as determined by ^{1}H NMR integration of the methyl doublet at 0.90 ppm but **154** was otherwise free of impurity. IR (neat film, cm^{-1}) 3418 (m, br), 2955 (m), 2862 (m), 1737 (s), 1437 (s), 1350 (m), 1236 (s), 1152 (s), 1049 (w), 1011 (m), 897 (w), 855 (w), 810 (w), 765 (w), 695 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37 (t of sextuplets, 1H, $J_{H3\text{-}H4}$ = 7.4 Hz, $J_{H1\text{-}H3} = J_{Me\text{-}H3}$ = 1.3 Hz, H_3), 3.99 (br s, 2H, H_1), 3.73 (s, 6H, $-OC\underline{H}_3$), 3.37 (t, 1H, $J_{H5\text{-}H6}$ = 7.4 Hz, H_6), 2.09 (q, 2H, $J_{H3\text{-}H4} = J_{H4\text{-}H5}$ = 7.4 Hz , H_4), 1.98 (q, 2H, $J_{H4\text{-}H5} = J_{H5\text{-}H6}$ = 7.4 Hz, H_5), 1.64 (s, 3H, $C_2\text{-}C\underline{H}_3$), 1.40 (broad s, 1H, $-O\underline{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 ($-\underline{C}O_2CH_3$), 136.6 (C_2), 123.8 (C_3), 68.6 (C_1), 52.5 ($-CO_2\underline{C}H_3$), 51.0 (C_6), 28.5 (C_4), 25.2 (C_5), 13.6 ($C_2\text{-}\underline{C}H_3$); HMQC (500 MHz, $CDCl_3$) δ 123.8 $\leftrightarrow$ δ 5.37; δ 68.6 $\leftrightarrow$ δ 3.99; δ 52.5 $\leftrightarrow$ δ 3.73; δ 51.0 $\leftrightarrow$ δ 3.37; δ 28.5 $\leftrightarrow$ δ 2.09; δ 25.2 $\leftrightarrow$ δ 1.98; δ 13.6 $\leftrightarrow$ δ 1.64. Analysis calculated for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; found: C, 57.51; H, 7.96.

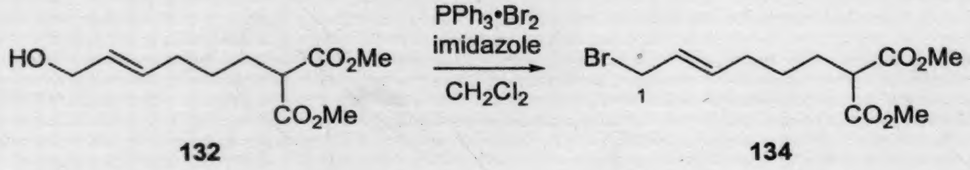


Dimethyl 6-hydroxy-5-methyl-4-hexenylmalonate (155): A round-bottom flask was charged with a solution of dimethyl 4-pentenylmalonate **143** (2.52 g, 12.6 mmol), methacrolein (2.50 mL, 30.2 mmol), and 2nd generation Grubbs catalyst (566.7 mg, 0.668 mmol, 5 mol %) in freshly distilled dichloromethane (50 mL). The faintly orange mixture was maintained at reflux for 3 hours under a very gentle stream of argon. After cooling, the solvent was removed *in vacuo* and replaced with methanol (~ 50 mL). The solution was cooled to -78 °C, and $CeCl_3 \cdot 7H_2O$ (5.45 g, 14.6 mmol) was added with rapid stirring. Over the course of 30 minutes, $NaBH_4$ (550.1 mg, 14.5 mmol) was carefully added in small portions to the rapidly-stirring solution while the temperature was maintained at -78 °C. During this time, a clumpy white precipitate began to form. Once addition was complete, the reaction was allowed to warm to room temperature, and stirring continued for an additional 30 minutes. The reaction mixture was then poured into saturated aqueous ammonium chloride (~ 100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over solid $CaCl_2$, filtered, and finally concentrated *in vacuo* to furnish crude **155** as a pale yellow oil. Silica gel chromatography of **155** with diethyl ether as eluent afforded **155** (1.76 g, 7.20 mmol, 57%) as a yellow oil. A small amount (~ 5%) of saturated analogue was present as an impurity in **155** as determined by ^{1}H NMR integration of the methyl doublet at 0.90 ppm but **155** was otherwise free of impurity. IR (neat film, cm^{-1}) 3418 (m, br), 2955 (m), 2862 (m), 1737 (s), 1437 (s), 1345 (m), 1273 (m),1226 (m), 1157 (m), 1061 (w), 1011 (m), 852 (w); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.38 (triplet of sextuplets, 1H, $J_{H3\text{-}H4}$ = 7.2 Hz, $J_{H1\text{-}H3}$ = $J_{Me\text{-}H3}$ = 1.3 Hz, H$_3$), 3.99 (s, 2H, H$_1$), 3.73 (s, 6H,-OCH$_3$), 3.36 (t, 1H, $J_{H6\text{-}H7}$ = 7.5 Hz, H$_7$), 2.07 (q, 2H, $J_{H3\text{-}H4}$ = $J_{H4\text{-}H5}$ = 7.2 Hz , H$_4$), 1.91 (q, 2H, $J_{H5\text{-}H6}$ = $J_{H6\text{-}H7}$ = 7.5 Hz, H$_6$), 1.65 (s, 3H, C$_2$-CH$_3$), 1.4 (broad s, 1H, -OH), 1.39 (m, 2H, $J_{H4\text{-}H5}$ = 7.2 Hz, $J_{H5\text{-}H6}$ = 7.5 Hz, H$_5$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 169.8 (-CO$_2$CH$_3$), 135.5 (C$_2$), 125.2 (C$_3$), 68.8 (C$_1$), 52.5 (-CO$_2$CH$_3$), 51.6 (C$_7$), 28.5 (C$_4$), 27.2 (C$_5$ or C$_6$), 27.1(C$_5$ or C$_6$), 13.7 (C$_2$-CH$_3$); HMQC (500 MHz, CDCl$_3$) δ 125.2 ↔ δ 5.39; δ 68.8 ↔ δ 3.99; δ 52.5 ↔ δ 3.73; δ 51.6 ↔ δ 3.36; δ 13.7 ↔ δ 1.65. Analysis calculated for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25; found: C, 58.50; H, 8.26.

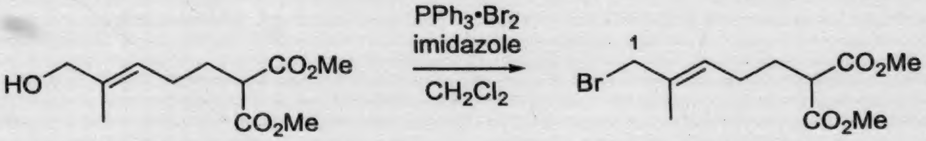


Dimethyl 5-Bromo-3-pentenylmalonate (133): A small round-bottom flask was charged with a solution of Br$_2$ (1.04 g, 6.52 mmol) in freshly distilled dichloromethane and then cooled to 0 °C. Solid triphenylphosphine (1.71g, 6.52 mmol) was then added, with rapid stirring, resulting in a suspension of a white solid in an off-white solution.

Over the course of 10 minutes, a solution of alcohol **131** (1.41 g, 6.52 mmol) and imidazole (0.4442 g, 6.52 mmol) in dichloromethane (5 mL) was added to the cooled solution of $PPh_3{\cdot}Br_2$. Once addition was complete, the resulting mixture was allowed to warm to room temperature and allowed to stir for an additional 30 minutes, at which point the bulk of the dichloromethane was removed *in vacuo*. Fresh dichloromethane (~ 10 mL) was added to the solid white residue, and the residue was transferred, with stirring and rinsing, onto a silica-gel column. Upon elution with dichloromethane, **133** was obtained as a yellow oil (1.34 g, 4.80 mmol, 74%). A small amount (~ 9%) of saturated analogue was present as an impurity in **133** as determined by ^{1}H NMR integration of the triplet at 3.65 ppm but **133** was otherwise free of impurity. IR (neat film, cm^{-1}) 3003 (w), 2954 (m), 2847 (w), 1736 (s),1661 (w), 1436 (m), 1341 (w), 1229 (m), 1207 (m), 1157 (m), 1049 (w), 967 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (m, 2H, H_2 and H_3), 3.92 (m, 2H, H_1), 3.74 (s, 6H,$-OC\underline{H}_3$), 3.37 (t, 1H, $J_{H5\text{-}H6} = 7.4$ Hz, H_6), 2.12 (m, 2H, $J_{H4\text{-}H5} = 7.4$ Hz, H_4), 2.00 (q, 2H, $J_{H4\text{-}H5} = J_{H5\text{-}H6} = 7.4$ Hz, H_5); ^{1}H-^{1}H GCOSY (500 MHz, $CDCl_3$) δ 5.72 $\leftrightarrow$ δ 3.92, δ 2.12; δ 3.92 $\leftrightarrow$ δ 2.12; δ 3.37 $\leftrightarrow$ δ 2.00; δ 2.12 $\leftrightarrow$ δ 2.00; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6 ($-\underline{C}O_2CH_3$), 134.0 (C_2 or C_3), 127.9 (C_2 or C_3), 52.5 ($-CO_2\underline{C}H_3$), 50.8 (C_6), 32.7 (C_1), 29.6 (C_4), 27.8(C_5); HMQC (500 MHz, $CDCl_3$) δ 134.0 $\leftrightarrow$ δ 5.72; δ 127.9 $\leftrightarrow$ δ 5.72; δ 52.5 $\leftrightarrow$ δ 3.74; δ 50.8 $\leftrightarrow$ δ 3.37; δ 32.7 $\leftrightarrow$ δ 3.92; δ 29.6 $\leftrightarrow$ δ 2.12; δ 27.8 $\leftrightarrow$ δ 2.00. Analysis calculated for $C_{10}H_{15}BrO_4$: C, 43.03; H, 5.42; found: C, 43.32; H, 5.54.

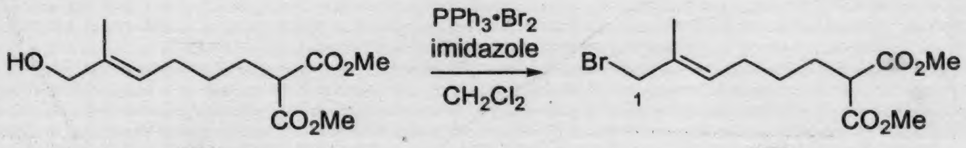


Dimethyl 6-Bromo-4-hexenylmalonate (134): A small round-bottom flask was charged with a solution of Br_2 (0.87 g, 5.44 mmol) in freshly distilled dichloromethane and then cooled to 0 °C. Solid triphenylphosphine (1.41 g, 5.38 mmol) was then added, with rapid stirring, resulting in a suspension of a white solid in an off-white solution. Over the course of 10 minutes, a solution of alcohol **132** (1.25 g, 5.43 mmol) and imidazole (370.1 mg, 5.44 mmol) in dichloromethane was added to the cooled solution of $PPh_3{\cdot}Br_2$. Once addition was complete, the resulting mixture was allowed to warm to room temperature and allowed to stir for an additional 30 minutes, at which point the bulk of the dichloromethane was removed *in vacuo*. Fresh dichloromethane (~ 10 mL) was added to the solid white residue, and the residue was transferred, with stirring and rinsing, onto a silica-gel column. Upon elution with dichloromethane, **134** was obtained as a yellow oil (1.19 g, 4.06 mmol, 75%). A small amount (~7%) of saturated analogue was present as an impurity in **134** as determined by ^{1}H NMR integration of the triplet at 3.39 ppm but **134** was otherwise free of impurity. IR (neat film, cm^{-1}) 3001 (w), 2954 (m), 2862 (w), 1753 (s), 1737 (s), 1661 (w), 1436 (m), 1345 (m), 1267 (m), 1241 (m), 1207 (m), 1157 (m), 1055 (w), 1014 (w), 968 (w), 909 (w), 834 (w), 788 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (m, 2H, H_2 and H_3), 3.93 (d, 2H, $J_{H1\text{-}H2}$ = 6.5 Hz, H_1), 3.74 (s, 6H,-OC$\underline{H}_3$), 3.35 (t, 1H, $J_{H6\text{-}H7}$ = 7.5 Hz, H_7), 2.10 (m, 2H, H_4), 1.90 (m, 2H, H_6), 1.42 (m, 2H, H_5). Analysis calculated for $C_{11}H_{17}BrO_4$: C, 45.07; H, 5.84; found: C, 44.85; H, 5.91.



154 156

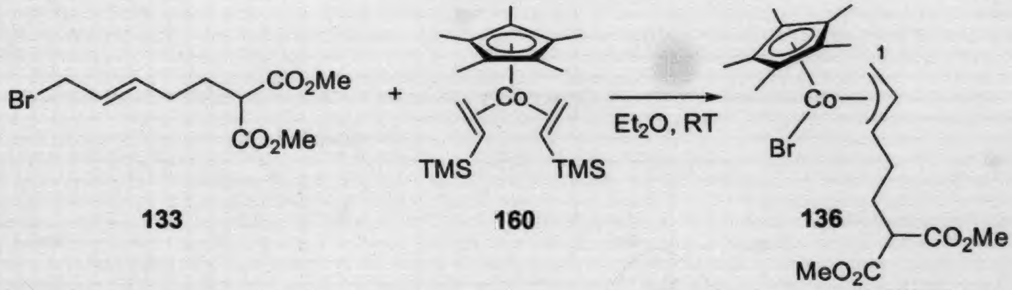
Dimethyl 5-Bromo-4-methyl-3-pentenylmalonate (156): A small round-bottom flask was charged with a solution of Br_2 (0.91 g, 5.69 mmol) in freshly distilled dichloromethane and then cooled to 0 °C. Solid triphenylphosphine (1.49 g, 5.68 mmol) was then added, with rapid stirring, resulting in a suspension of a white solid in an off-white solution. Over the course of 10 minutes, a solution of alcohol **154** (1.31 g, 5.69 mmol) and imidazole (0.3875 g, 5.69 mmol) in dichloromethane (5 mL) was added to the cooled solution of $PPh_3{\cdot}Br_2$. Once addition was complete, the resulting mixture was allowed to warm to room temperature and allowed to stir for an additional 30 minutes, at which point the bulk of the dichloromethane was removed *in vacuo*. Fresh dichloromethane (~ 10 mL) was added to the solid white residue, and the residue was transferred, with stirring and rinsing, onto a silica-gel column. Upon elution with dichloromethane, **156** was obtained as a yellow oil (1.15 g, 3.92 mmol, 69%). A small amount (~ 3%) of saturated analogue was present as an impurity in **156** as determined by ^{1}H NMR integration of the methyl doublet signal at 1.01 ppm but **156** was otherwise free of impurity. IR (neat film, cm^{-1}) 2954 (m), 1752 (s), 1737 (s), 1670 (w), 1436 (m), 1348 (m), 1206 (m), 1152 (m), 1082 (w), 1044 (w), 1008 (w), 899 (w), 812 (w), 762 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (t, 1H, $J_{H3\text{-}H4}$ = 7.2 Hz, H_3), 3.95 (s, 2H, H_1), 3.75 (s, 6H,-OC$\underline{H}_3$), 3.37 (t, 1H, $J_{H5\text{-}H6}$ = 7.4 Hz, H_6), 2.09 (q, 2H, $J_{H3\text{-}H4}$ = $J_{H4\text{-}H5}$ = 7.4 Hz , H_4), 1.99 (q, 2H, $J_{H4\text{-}H5}$ = $J_{H5\text{-}H6}$ = 7.4 Hz, H_5), 1.74 (s, 3H, C_2-C$\underline{H}_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 169.6 (-$\underline{C}O_2CH_3$), 133.8 (C_2), 129.1 (C_3), 52.5 (-$CO_2\underline{C}H_3$), 50.9 (C_6), 41.0 (C_1), 28.1 (C_5), 25.9 (C_4), 14.6 (C_2-$\underline{C}H_3$); HMQC (300 MHz, CDCl$_3$) δ 129.1 ↔ δ 5.56; δ 52.5 ↔ δ 3.75; δ 50.9 ↔ δ 3.34; δ 41.0 ↔ δ 3.95; δ 28.1 ↔ δ 1.99; δ 25.9 ↔ δ 2.08, δ 14.6 ↔ δ 1.74. Analysis calculated for $C_{11}H_{17}BrO_4$: C, 45.07; H, 5.84; found: C, 45.25; H, 5.88.



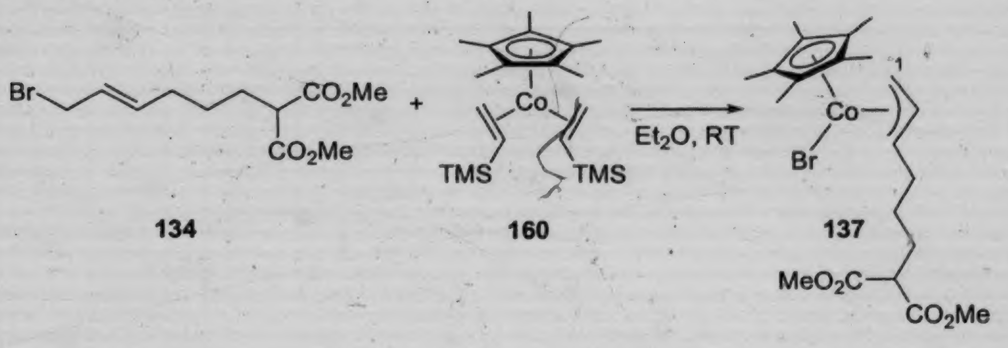
155 **157**

Dimethyl 6-Bromo-5-methyl-4-hexenylmalonate (157): A small round-bottom flask was charged with a solution of Br_2 (0.95 g, 5.94 mmol) in freshly distilled dichloromethane and then cooled to 0 °C. Solid triphenylphosphine (1.56 g, 5.95 mmol) was then added, with rapid stirring, resulting in a suspension of a white solid in an off-white solution. Over the course of 10 minutes, a solution of alcohol **155** (1.45 g, 5.94 mmol) and imidazole (403.5 mg, 5.93 mmol) in dichloromethane (5 mL) was added to the cooled solution of $PPh_3 \cdot Br_2$. Once addition was complete, the resulting mixture was allowed to warm to room temperature and allowed to stir for an additional 30 minutes, at which point the bulk of the dichloromethane was removed *in vacuo*. Fresh dichloromethane (~ 10 mL) was added to the solid white residue, and the residue was transferred, with stirring and rinsing, onto a silica-gel column. Upon elution with dichloromethane, **157** was obtained as a yellow oil (1.28 g, 4.17 mmol, 70%). A small amount (~3 %) of saturated analogue was present as an impurity in **157** as determined by

^{1}H NMR integration of the methyl triplet at 1.00 ppm but **157** was otherwise free of impurity. IR (neat film, cm^{-1}) 2953 (w), 2861 (m), 1753 (m), 1736 (s), 1435 (w), 1343 (w), 1271 (w), 1207 (m), 1150 (m), 1055 (w), 1009 (w), 847 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (t, 1H, J_{H3-H4} = 7.3 Hz, H_3), 3.95 (s, 2H, H_1), 3.74 (s, 6H,-$OC\underline{H}_3$), 3.35 (t, 1H, J_{H6-H7} = 7.5 Hz, H_7), 2.06 (q, 2H, J_{H3-H4} = J_{H4-H5} = 7.3 Hz, H_4), 1.90 (m, 2H, H_6), 1.74 (s, 3H, C_2-$C\underline{H}_3$), 1.39 (m, 2H, H_5); ^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) δ 5.56 ↔ δ 3.95, δ 2.06, δ 1.74; δ 3.95 ↔ δ 2.06; δ 3.35 ↔ δ 1.90; δ 2.06 ↔ δ 1.74, δ 1.39; δ 1.90 ↔ δ 1.39; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (-$\underline{C}O_2CH_3$), 132.7 (C_2),130.3 (C_3), 52.5 (-$CO_2\underline{C}H_3$), 51.5 (C_7), 41.5 (C_1), 28.4 (C_6), 27.8 (C_4), 26.8 (C_5), 14.7 (C_2-$\underline{C}H_3$); HMQC (500 MHz, $CDCl_3$) δ 130.3 ↔ δ 5.56; δ 52.5 ↔ δ 3.74; δ 51.5 ↔ δ 3.35; δ 41.5 ↔ δ 3.95; δ 28.4 ↔ δ 1.90; δ 27.8 ↔ δ 2.06; δ 26.8 ↔ δ 1.39; δ 14.7 ↔ δ 1.74. An NOE interaction was detected between the signals at δ 3.95 and δ 5.56 in a ROESY experiment (300 MHz, acetone-d_6). Analysis calculated for $C_{12}H_{19}BrO_4$: C, 46.92; H, 6.23; found: C, 47.06; H, 6.35.

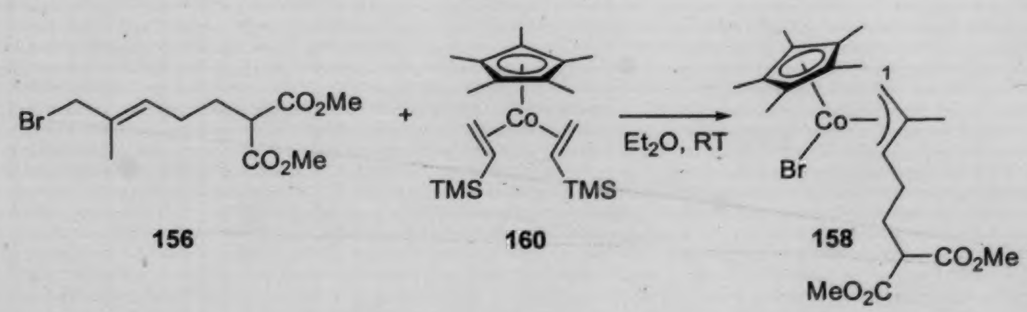


Cp*Co(III) 1-(Dimethyl 2-ethylmalonate)allyl bromide (136): A small vial was charged with neat allyl halide **133** (217.1 mg, 0.778 mmol) and a stir-bar. A solution of Cp*Co(I) bis(vinyltrimethylsilane) **160** (279.0 mg, 0.707 mmol) in diethyl ether (~ 2 ml) was then added, and the resulting solution quickly became purple in colour. The reaction was stirred at room temperature for 15 minutes and then filtered through a plug of Celite to separate a small amount of insoluble blue-green material. The deep-purple solution was then concentrated to dryness, and the resulting purple residue was redissolved in a few drops of diethyl ether. The purple solution was transferred via pipette to a small vial containing pentane (~ 1mL), using a minimal amount of diethyl ether rinse to ensure complete transfer. The purple solution was then cooled overnight at -34 °C, and the faintly pink purple supernatant solution was then decanted to furnish Cp*Co(III) allyl complex **136** (239.5 mg, 0.506 mmol, 72%) as a purple powder which was dried under high-vacuum. IR (microscope, cm^{-1}) 3449 (w), 3075 (m), 2961 (s), 2402 (w), 2055 (w), 1964 (w), 1729 (m), 1513 (m), 1425 (m), 1379 (m), 1333 (m), 1311 (w), 1280 (m), 1252 (m), 1219 (m), 1147 (m), 1072 (m), 1013 (m), 985 (m), 963 (m), 929 (w), 895 (m), 884 (m), 831 (w), 814 (m), 786 (m), 730 (m), 696 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 3.57 (d, 1H, $J_{H1syn\text{-}H2}$ = 7.1 Hz, H_{1syn}), 3.52 (m, 3H, H_2, H_3, and H_6), 3.33 (s, 3H, -OC$\underline{H}_3$), 3.32 (s, 3H, -OC$\underline{H}_3$), 3.20 (d, 1H, $J_{H1anti\text{-}H2}$ = 11.5 Hz, H_{1anti}), 2.24 (m, 2H, H_5), 2.06 (m, 1H, H_{4a}), 1.70 (app. dq, 1H, $J_{H4a\text{-}H4b}$ = 13.2 Hz, $J_{H3anti\text{-}H4b} = J_{H4b\text{-}H5}$ = 7.6 Hz, H_{4b}), 1.29 (s, 15H, $C_5\underline{Me}_5$); ^{1}H-^{1}H GCOSY (500 MHz, C_6D_6) δ 3.57 $\leftrightarrow$ δ 3.52; δ 3.52 $\leftrightarrow$ δ 3.20, δ 2.24, δ 2.06, δ 1.70; δ 2.24 $\leftrightarrow$ δ 2.06, δ 1.70; δ 2.06 $\leftrightarrow$ δ 1.70; ^{13}C NMR (125 MHz, C_6D_6) δ 169.7 (-$\underline{C}O_2CH_3$), 95.9 (C_2), 93.3 ($\underline{C}_5Me_5$), 75.0 (C_3), 54.7 (C_1), 51.9 (C_6 or -O$\underline{C}H_3$), 51.1 (C_6 or -O$\underline{C}H_3$), 31.1 (C_4 or C_5), 29.6 (C_4 or C_5), 10.0 ($C_5\underline{Me}_5$).



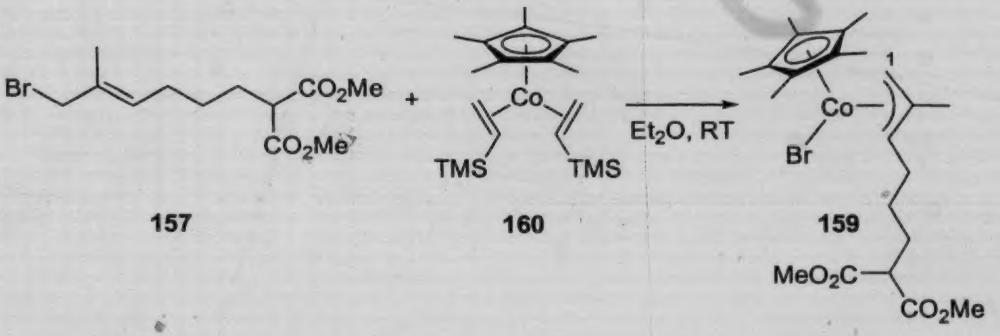
Cp*Co(III) 1-(Dimethyl 3-propylmalonate)allyl bromide (137): A small vial was charged with neat allyl halide **134** (225.6 mg, 0.770 mmol) and a stir-bar. A solution of Cp*Co(I) bis(vinyltrimethylsilane) **160** (276.1mg, 0.700 mmol) in diethyl ether (~ 2 ml) was then added, and the resulting solution quickly became purple in colour. The reaction was stirred at room temperature for 15 minutes and then filtered through a plug of Celite to separate a small amount of insoluble blue-green material. The deep-purple solution was then concentrated to dryness, and the resulting purple residue was redissolved in a few drops of diethyl ether. The purple solution was transferred via pipette to a small vial containing pentane (~ 1mL), using a minimal amount of diethyl ether rinse to ensure complete transfer. The purple solution was then cooled overnight at -34 °C, and the faintly pink purple supernatant solution was then decanted to furnish Cp*Co(III) allyl complex **137** (249.1 mg, 0.511 mmol, 73%) as a purple powder which was dried under high-vacuum. IR (microscope, cm^{-1}) 3462 (w), 3068 (m), 2952 (m), 2513 (w), 1968 (w),1861 (w), 1723 (m), 1604 (m), 1515 (m), 1495 (m), 1434 (s), 1383 (m), 1305 (m), 1356 (m), 1323 (m), 1267 (m), 1208 (m), 1147 (m), 1111 (m), 1069 (m), 1029 (m), 1001 (m), 987 (m), 972 (m), 902 (m), 864 (m), 831 (m), 804 (m), 754 (w), 734 (m), 697 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 3.61 (m, 1H, H_3), δ 3.56 (d, 1H, $J_{H1syn\text{-}H2}$ = 7.3 Hz,

H_{1syn}), 3.36 (m, 2H, H_2 and H_7), 3.34 (s, 3H, -$OC\underline{H}_3$), 3.32 (s, 3H, -$OC\underline{H}_3$), 3.19 (d, 1H, $J_{H1anti\text{-}H2}$ = 12.3 Hz, H_{1anti}), 2.14 (m, 1H, H_{6a}), 2.07 (m, 1H, H_{6b}), 1.95 (m, 1H, H_{4a}), 1.58 (m, 1H, H_{5a}), 1.46 (m, 2H, H_{4b} and H_{5b}), 1.28 (s, 15H, $C_5\underline{Me}_5$); ^{1}H-^{1}H GCOSY (500 MHz, C_6D_6) δ 3.61 ↔ δ 3.36, δ 1.95, δ 1.46; δ 3.56 ↔ δ 3.36; δ 3.36 ↔ δ 3.19, δ 2.14, δ 2.07; δ 2.14 ↔ δ 2.07, δ 1.58, δ 1.46; δ 2.07 ↔ δ 1.58, δ 1.46; δ 1.95 ↔ δ 1.46; δ 1.58 ↔ δ 1.46; ^{13}C NMR (125 MHz, C_6D_6) δ 169.7 (-$\underline{C}O_2CH_3$), 95.8 (C_2), 93.1 ($\underline{C}_5Me_5$), 76.7 (C_3), 54.2 (C_1), 52.0 (C_7 or -$O\underline{C}H_3$), 51.9 (C_7 or -$O\underline{C}H_3$), 33.6 (C_4, C_5, or C_6), 29.0(C_4, C_5, or C_6), 28.7 (C_4, C_5, or C_6), 10.0 ($C_5\underline{Me}_5$).



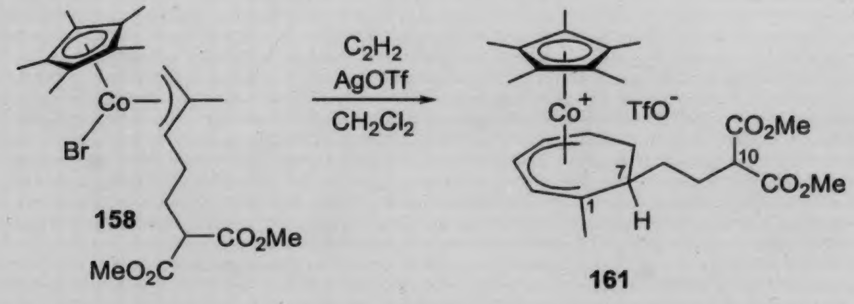
156 **160** **158**

Cp*Co(III) 1-(Dimethyl 2-ethylmalonate)-2-methylallyl bromide (158): A small vial was charged with neat allyl halide **156** (217.6 mg, 0.742 mmol) and a stir-bar. A solution of Cp*Co(I) bis(vinyltrimethylsilane) **160** (266.5 mg, 0.675 mmol) in diethyl ether (~ 2 ml) was then added, and the resulting solution quickly became purple in colour. The reaction was stirred at room temperature for 15 minutes and then filtered through a plug of Celite to separate a small amount of insoluble blue-green material. The deep-purple solution was then concentrated to dryness, and the resulting purple residue was redissolved in a few drops of diethyl ether. The purple solution was transferred via pipette to a small vial containing pentane (~ 1mL), using a minimal amount of diethyl ether rinse to ensure complete transfer. The purple solution was then cooled overnight at -34 °C, and the faintly pink-purple supernatant solution was then decanted to furnish Cp*Co(III) allyl complex **158** (228.6 mg, 0.469 mmol, 69%) as a purple powder which was dried under high-vacuum. IR (microscope, cm^{-1}) 3461 (w), 2995 (m), 2956 (m), 2908 (m), 1742 (s), 1603 (w), 1507 (w), 1436 (m), 1379 (m), 1355 (m), 1305 (m), 1281 (m), 1250 (m), 1197 (m), 1162 (m), 1121 (w), 1084 (m), 1054 (m), 1025 (m), 982 (w), 968 (w), 907 (w), 887 (w), 877 (w), 849 (w), 797 (w), 766 (w), 735 (w), 697 (w); ^{1}H NMR (500 MHz, C_6D_6) δ 3.59 (t, 1H, $J_{H3\text{-}H4a} = J_{H3\text{-}H4b} = 7.4$ Hz, H_3), 3.53 (t, 1H, $J_{H5\text{-}H6} = 7.2$ Hz, H_6), 3.48 (s, 1H, H_{1syn}), 3.33 (s, 3H,-OC$\underline{H}_3$), 3.32 (s, 3H,-OC$\underline{H}_3$), 3.27 (s, 1H, H_{1anti}), 2.28 (m, 2H, H_5), 2.04 (m, 1H, H_{4a}), 1.84 (m,1H, H_{4b}), 1.48 (s, 3H, C_2-$\underline{Me}$), 1.30 (s, 15H, $C_5\underline{Me}_5$); ^{1}H-^{1}H GCOSY (500 MHz, C_6D_6) δ 3.59 ↔ δ 3.48, δ 3.27, δ 2.04, δ 1.84, δ 1.48; δ 3.53 ↔ δ 2.28; δ 2.28 ↔ δ 2.04, δ 1.84; δ 2.04 ↔ δ 1.84; ^{13}C NMR (125 MHz, C_6D_6) δ 169.7 (-$\underline{C}O_2CH_3$), 106.7 (C_2), 93.3 ($\underline{C}_5Me_5$), 68.1 (C_3), 52.9 (C_1), 51.9 (-O$\underline{C}H_3$), 51.6 (C_6), 28.4 (C_4 or C_5), 28.0 (C_4 or C_5), 17.9 (C_2-$\underline{Me}$), 10.3 ($C_5\underline{Me}_5$); HMQC (300 MHz, C_6D_6) δ 68.1 ↔ δ 3.59; δ 52.9 ↔ δ 3.48, δ 3.27; δ 51.9 ↔ δ 3.32, δ 3.33; δ 51.6 ↔ δ 3.53; δ 28.4 ↔ δ 2.28, δ 2.04 and/or δ 1.84; δ 28.0 ↔ δ 2.28, δ 2.04 and/or δ 1.84; δ 17.9 ↔ δ 1.48; δ 10.3 ↔ δ 1.30. HMBC (300 MHz, C_6D_6) δ 169.7 ↔ δ 3.53, δ 3.33, δ 3.32; δ 106.7 ↔ δ 1.48; δ 93.3 ↔ δ 1.30; δ 68.1 ↔ δ 1.48; δ 52.9 ↔ δ 1.48.

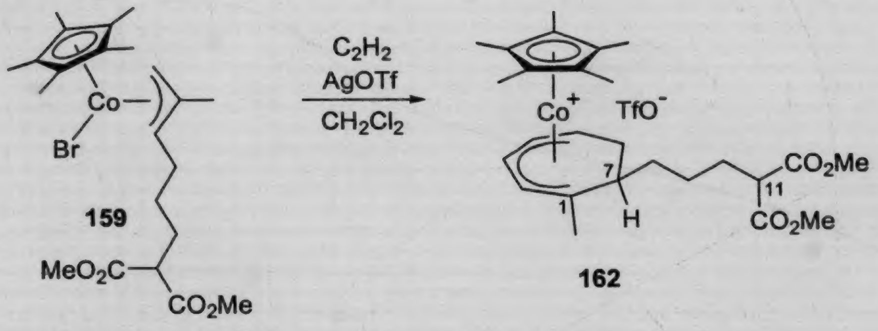


Cp*Co(III) 1-(Dimethyl 3-propylmalonate)-2-methylallyl bromide (159): A small vial was charged with neat allyl halide **157** (233.8 mg, 0.759 mmol) and a stir-bar. A solution of Cp*Co(I) bis(vinyltrimethylsilane) **160** (272.9 mg, 0.692 mmol) in diethyl ether (~ 2 ml) was then added, and the resulting solution quickly became purple in colour. The reaction was stirred at room temperature for 15 minutes and then filtered through a plug of Celite to separate a small amount of insoluble blue-green material. The deep-purple solution was then concentrated to dryness, and the resulting purple residue was redissolved in a few drops of diethyl ether. The purple solution was transferred via pipette to a small vial containing pentane (~ 1mL), using a minimal amount of diethyl ether rinse to ensure complete transfer. The purple solution was then cooled overnight at -34 °C, and the faintly pink-purple supernatant solution was then decanted to furnish Cp*Co(III) allyl complex **159** (270.2 mg, 0.539 mmol, 78%) as a purple powder which was dried under high-vacuum. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, -40 °C) δ 3.68 (s, 6H,-OC$\underline{H}_3$), 3.67 (s, 1H, H$_{1syn}$), 3.41 (t, 1H, $J_{H6\text{-}H7}$ = 7.8 Hz, H$_7$), 3.02 (t, 1H, $J_{H3\text{-}H4a}$ = $J_{H3\text{-}H4b}$ = 7.3 Hz, H$_3$), 2.63 (s, 1H, H$_{1anti}$), 2.04 (m, 1H, H$_{4a}$), 1.98 (app. q, 2H, $J_{H5a\text{-}H6}$ = $J_{H5b\text{-}H6}$ = $J_{H6\text{-}H7}$ = 7.9 Hz, H$_6$), 1.85 (m,1H, H$_{4b}$), 1.75 (s, 3H, C$_2$-$\underline{Me}$), 1.59 (m,1H, H$_{5a}$), ~1.50 (m,1H, obscured by the signal at δ 1.48, H$_{5b}$), 1.48 (s, 15H, C$_5\underline{Me}_5$); ^{1}H-^{1}H GCOSY (400

MHz, CD_2Cl_2, -40 °C) δ 3.41 ↔ δ 1.98; δ 3.02 ↔ δ 2.04, δ 1.85; δ 2.04 ↔ δ 1.85, δ 1.59; δ 1.98 ↔ δ 1.59; δ 1.85 ↔ δ 1.59; ^{13}C NMR (100 MHz, CD_2Cl_2, -40 °C) δ 169.8 (-CO_2CH_3), 106.7 (C_2), 93.2 (C_5Me_5), 68.6 (C_3), 52.7 (two peaks, C_1 and C_7), 51.3 (-OCH_3), 29.6 (C_4, C_5, or C_6), 28.8 (C_4, C_5, or C_6), 27.0 (C_4, C_5, or C_6), 18.0 (C_2-Me), 10.2 (C_5Me_5).

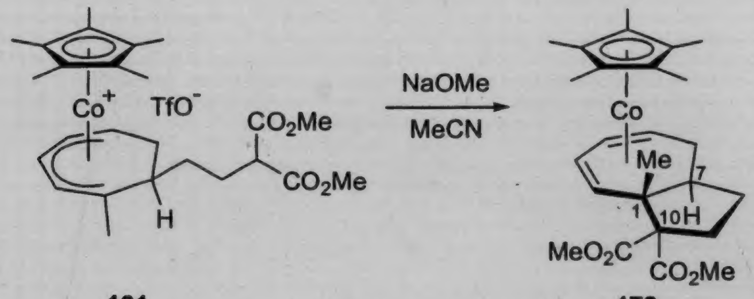


Cp*Co(III) 1-methyl-7-(dimethyl 2-ethylmalonate)cycloheptadienyl trifluoromethanesulfonate (161): A glass vial was charged with silver triflate (22.3 mg, 0.0868 mmol) in the glove box and fitted with a stir bar and a rubber septum. A second vial was then charged with Cp*Co(III) allyl bromide **158** (36.8 mg, 0.0755 mmol) and a septum, and then both vials were removed to the fume hood and cooled to -78 °C under an argon atmosphere. The silver triflate was suspended at -78 °C in degassed dichloromethane (10 mL) which was added via stainless steel cannula, and a stream of acetylene was introduced to this suspension with a vent to a mercury bubbler. After several minutes, the Cp*Co(III) allyl bromide was dissolved in several milliliters of dichloromethane at -78 °C, and the resulting purple solution was transferred via cannula into the silver triflate suspension. The resulting mixture was allowed to gradually warm to room temperature overnight under an acetylene atmosphere, and the resulting red/brown solution was concentrated *in vacuo*. The residue was chromatographed on silica gel with 4% methanol in dichloromethane, and **161** was collected as a red-orange fraction. Removal of solvent and drying under vacuum afforded **161** (30.8 mg, 0.0506 mmol, 67%) as a red-orange gum. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.49 (app. t, 1H, $J_{H2\text{-}H3}$ = 6.2 Hz, $J_{H3\text{-}H4}$ = 6.8 Hz, H_3), 5.13 (d, 1H, $J_{H2\text{-}H3}$ = 6.2 Hz, H_2), 4.75 (app. t, 1H, $J_{H3\text{-}H4}$ = 6.8 Hz, $J_{H4\text{-}H5}$ = 8.7 Hz, H_4), 4.22 (dt, 1H, $J_{H4\text{-}H5}$ = 8.7 Hz, $J_{H5\text{-}H6a}$ = $J_{H5\text{-}H6b}$ = 4.2 Hz, H_5), 3.71 (s, 3H,$-OC\underline{H}_3$), 3.69 (s, 3H,$-OC\underline{H}_3$), 3.30 (t, 1H, $J_{H9\text{-}H10}$ = 7.0 Hz, H_{10}), 2.33 (ddd, 1H, $J_{H5\text{-}H6a}$ = 4.2 Hz, $J_{H6a\text{-}H6b}$ = 15.9 Hz, $J_{H6a\text{-}H7}$ = 9.2 Hz, H_{6a}), 1.85 (m (obscured by impurity), 1H, $J_{H5\text{-}H6b}$ = 4.2 Hz, $J_{H6a\text{-}H6b}$ = 15.9 Hz, H_{6b}), 1.78 (s, 15H, $C_5\underline{Me}_5$), 1.72 (m, 1H, H_{9a}), 1.59 (m, 2H, H_{8a} and H_{9b}), 1.47 (s, 3H, $C_1\text{-}\underline{Me}$), 1.33 (m,1H, H_{8b}), 0.65 (m, 1H, $J_{H6a\text{-}H7}$ = 9.2 Hz, H_7); ^{1}H-^{1}H GCOSY (300 MHz, CD_2Cl_2) δ 6.49 ↔ δ 5.13, δ 4.75, δ 4.22; δ 5.13 ↔ δ 1.47, δ 0.65; δ 4.75 ↔ δ 4.22, δ 1.85; δ 4.22 ↔ δ 2.33, δ1.85; δ 3.30 ↔ δ 1.72, δ 1.59; δ 2.33 ↔ δ 1.85, δ 0.65; δ 1.85 ↔ δ 0.65; δ 1.72 ↔ δ 1.59, δ 1.33; δ 1.59 ↔ δ 1.33, δ0.65; δ 1.33 ↔ δ 0.65; ^{13}C NMR (125 MHz, CD_2Cl_2) δ 169.7 ($-\underline{C}O_2CH_3$), 114.2 (C_1), 98.4 (C_3), 98.2 ($\underline{C}_5Me_5$), 97.8 (C_2 or C_4), 97.1 (C_2 or C_4), 84.7 (C_5), 52.8 ($-O\underline{C}H_3$), 51.7 (C_{10}), 45.4 (C_6 or C_7), 45.3 (C_6 or C_7), 29.9 (C_8), 27.7 (C_9), 23.3 ($C_1\text{-}\underline{Me}$), 9.6 ($C_5\underline{Me}_5$).



Cp*Co(III) 1-methyl-7-(dimethyl 3-propylmalonate)cycloheptadienyl trifluoromethanesulfonate (162): A glass vial was charged with silver triflate (27.1 mg, 0.105 mmol) in the glove box and fitted with a stir bar and a rubber septum. A second vial was then charged with Cp*Co(III) allyl bromide **159** (45.2 mg, 0.0902 mmol) and a septum, and then both vials were removed to the fume hood and cooled to -78 °C under an argon atmosphere. The silver triflate was suspended at -78 °C in degassed dichloromethane (10 mL) which was added via stainless steel cannula, and a stream of acetylene was introduced to this suspension with a vent to a mercury bubbler. After several minutes, the Cp*Co(III) allyl bromide was dissolved in several milliliters of dichloromethane at -78 °C, and the resulting purple solution was transferred via cannula into the silver triflate suspension. The resulting mixture was allowed to gradually warm to room temperature overnight under an acetylene atmosphere, and the resulting red/brown solution was concentrate *in vacuo*. The residue was chromatographed on silica gel with 4% methanol in dichloromethane, and **162** was collected as a red-orange fraction. Removal of solvent and drying under vacuum afforded **162** (33.1 mg, 0.0532 mmol, 59%) as a red-orange gum. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.68 (app. t, 1H, $J_{H2\text{-}H3}$ = 6.2 Hz, $J_{H3\text{-}H4}$ = 7.0 Hz, H$_3$), 5.25 (d, 1H, $J_{H2\text{-}H3}$ = 6.2 Hz, H$_2$), 4.81 (app. t, 1H, $J_{H3\text{-}H4}$ =

7.0 Hz, $J_{H4\text{-}H5}$ = 8.8 Hz, H_4), 4.21 (dt, 1H, $J_{H4\text{-}H5}$ = 8.8 Hz, $J_{H5\text{-}H6a}$ = $J_{H5\text{-}H6b}$ = 4.1 Hz, H_5), 3.70 (s, 6H,-OC$\underline{H}_3$), 3.27 (t, 1H, $J_{H10\text{-}H11}$ =7.4 Hz, H_{11}), 2.29 (ddd, 1H, $J_{H5\text{-}H6a}$ = 4.1 Hz, $J_{H6a\text{-}H6b}$ = 16.1 Hz, $J_{H6a\text{-}H7}$ = 9.7 Hz, H_{6a}), 1.96 (m (obscured by impurity), 1H, $J_{H5\text{-}H6b}$ = 4.1 Hz, $J_{H6a\text{-}H6b}$ = 16.1 Hz, H_{6b}), 1.80 (s, 15H, $C_5\underline{Me}_5$), 1.77 (m (obscured by $C_5\underline{Me}_5$ signal), 2H, H_{10}), 1.52 (m, 1H, H_{8a}), 1.43 (s, 3H, C_1-$\underline{Me}$), 1.30 (m,1H, H_{8b}), 1.16 (m,1H, H_{9a}), 1.00 (m,1H, H_{9b}), 0.53 (m, 1H, $J_{H6a\text{-}H7}$ = 9.7 Hz, H_7); ^{1}H-^{1}H GCOSY (400 MHz, CDCl$_3$) δ 6.68 ↔ δ 5.25, δ 4.81, δ 4.21; δ 5.25 ↔ δ 4.81, δ 1.43, δ 0.53; δ 4.81 ↔ δ 4.21, δ 1.96; δ 4.21 ↔ δ 2.29, δ 1.96; δ 3.27 ↔ δ 1.77; δ 2.29 ↔ δ 1.96, δ 0.53; δ 1.96 ↔ δ 0.53; δ 1.77 ↔ δ 1.16, δ1.00; δ 1.52 ↔ δ 1.30, δ 1.16, δ 1.00, δ 0.53; δ 1.30 ↔ δ 1.16, δ 1.00, δ 0.53; δ 1.16 ↔ δ 1.00; ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.6 (-$\underline{C}O_2CH_3$), 169.5 (-$\underline{C}O_2CH_3$), 113.7 (C_1), 98.2 (C_3), 97.7 ($\underline{C}_5Me_5$), 97.4 (C_2 or C_4), 97.2 (C_2 or C_4), 84.1 (C_5), 52.5 (-O$\underline{C}H_3$), 51.3 (C_{11}), 46.1 (C_6 or C_7), 43.7 (C_6 or C_7), 31.4 (C_8, C_9, or C_{10}), 28.6 (C_8, C_9, or C_{10}), 25.9 (C_8, C_9, or C_{10}), 22.8 (C_1-$\underline{Me}$), 9.4 ($C_5\underline{Me}_5$).

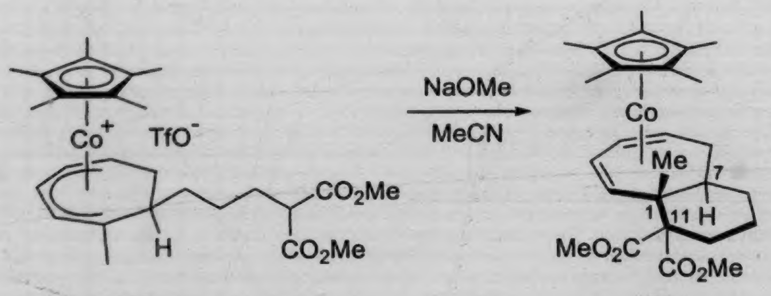


161 **172**

Cp*Co(I) η^4-8,8-dimethoxycarbonyl-7-methylbicyclo[5.3.0]deca-3,5-diene (172): In the glovebox, a vial was charged with a solution of cycloheptadienyl complex **161** (27.9 mg, 0.0458 mmol) in acetonitrile (3 mL). Powdered sodium methoxide (10.2

mg, 0.189 mmol) was suspended in this solution which was then stirred at room temperature for 30 minutes. The acetonitrile was removed *in vacuo*, and the red residue was dissolved in the minimum amount of pentane (~ 5 mL) and then eluted through a short plug of alumina (activity IV). The ruby red pentane solution was cooled to -34 °C, and **172** (16.8 mg, 0.0366 mmol) was harvested as deep red crystals suitable for X-ray crystallography. For full crystallographic data, request report #JMS0312 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3004 (w), 2992 (w), 2981 (w), 2964 (m), 2867 (s), 2831 (s), 1748 (w), 1729 (s), 1449 (w), 1432 (m), 1380 (w), 1346 (w), 1258 (w), 1246 (m), 1232 (m), 1197 (m), 1153 (w), 1132 (w), 1093 (w), 1079 (w), 1067 (w), 1031 (w), 913 (w), 726 (w); ^{1}H NMR (500 MHz, C_6D_6) δ 4.02 (dd, 1H, $J_{H2\text{-}H3}$ = 6.9 Hz, $J_{H3\text{-}H4}$ = 4.7 Hz, H_3), 3.83 (dd, 1H, $J_{H3\text{-}H4}$ = 4.7 Hz, $J_{H4\text{-}H5}$ = 7.1 Hz, H_4), 3.46 (s, 3H,$\text{-OC}\underline{\text{H}_3}$), 3.38 (s, 3H,$\text{-OC}\underline{\text{H}_3}$), 3.17 (d, 1H, $J_{H2\text{-}H3}$ = 6.9 Hz, H_2), 2.34 (m, 1H, H_{9a}), 2.23 (ddd, 1H, $J_{H8(a\text{ or }b)\text{-}H9b}$ = 11.5 Hz, $J_{H8(a\text{ or }b)\text{-}H9b}$ = 3.4 Hz, $J_{H9a\text{-}H9b}$ = 14.6 Hz, H_{9b}), 2.17 (app. br. t, 1H, $J_{H4\text{-}H5}$ = 7.1 Hz, $J_{H5\text{-}H6a}$ = 5.8 Hz, H_5), 1.65 (s, 15H, $C_5\underline{Me_5}$), 1.56 (m, 1H, H_{8a}), 1.51 (m, 1H, H_7), 1.36 (dddd, 1H, $J_{H5\text{-}H6a}$ = 5.8 Hz, $J_{H6a\text{-}H6b}$ = 16.2, $J_{H6a\text{-}H7}$ = 3.4 Hz, $^4J_{H5\text{-}(H4,\ H8a,\text{ or }H8b)}$ = 0.8 Hz, H_{6a}), 1.23 (s, 3H, $C_1\text{-}\underline{Me}$), 1.12 (m,2H, H_{6b} and H_{8b}); ^{1}H-^{1}H GCOSY (500 MHz, C_6D_6) δ 4.02 ↔ δ 3.83, δ 3.17; δ 3.83 ↔ δ 2.17; δ 3.17 ↔ δ 1.23; δ 2.34 ↔ δ 2.23, δ 1.56, δ 1.12; δ 2.23 ↔ δ 1.56, δ 1.12; δ 2.17 ↔ δ 1.36, δ 1.12; δ 1.56 ↔ δ 1.51, δ 1.12; ^{13}C NMR (125 MHz, C_6D_6) δ 172.4 ($\text{-}\underline{C}O_2CH_3$), 171.6 ($\text{-}\underline{C}O_2CH_3$), 89.4 ($\underline{C_5}Me_5$), 82.4 ($C_3$), 81.4 ($C_4$), 67.9 ($C_{10}$), 59.4 ($C_2$), 53.7 ($C_5$), 51.7 ($\text{-O}\underline{C}H_3$), 51.3 ($\text{-O}\underline{C}H_3$), 50.6 ($C_1$), 39.6 ($C_7$), 29.4 ($C_9$), 29.0 ($C_6$), 26.4 ($C_8$), 19.7 ($C_1\text{-}\underline{Me}$), 10.0 ($C_5\underline{Me_5}$); HMQC (500 MHz, C_6D_6) δ 82.4 ↔ δ 4.02; δ 81.4 ↔ δ 3.83; δ 59.4 ↔ δ 3.17; δ 53.7 ↔ δ 2.17; δ 51.7 ↔ δ 3.38; δ 51.3 ↔ δ

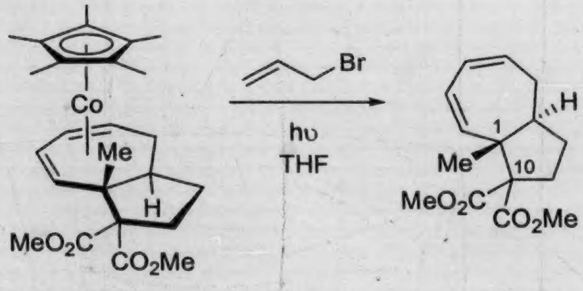
3.46; δ 39.6 ↔ δ 1.51; δ 29.4 ↔ δ 2.34, δ 2.23; δ 29.0 ↔ δ 1.36, δ 1.12; δ 26.4 ↔ δ 1.56, δ 1.12; δ 19.7 ↔ δ 1.23; δ 10.0 ↔ δ 1.65. Analysis calculated for $C_{25}H_{35}CoO_4$: C, 65.49; H, 7.69; found: C, 65.35; H, 7.86.



162 173

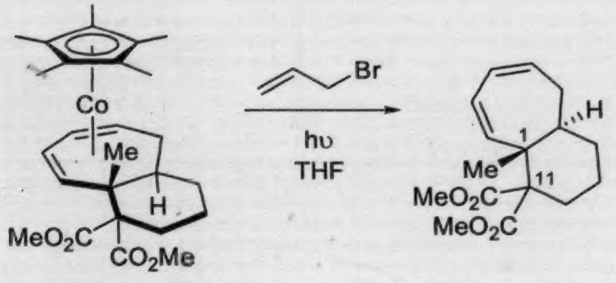
Cp*Co(I) η^4-8,8-dimethoxycarbonyl-7-methylbicyclo[5.4.0]undeca-3,5-diene (173): In the glovebox, a vial was charged with a solution of cycloheptadienyl complex **162** (30.0 mg, 0.0482 mmol) in acetonitrile. Powdered sodium methoxide (12.1 mg, 0.224 mmol) was suspended in this solution which was then stirred at room temperature for 30 minutes. The acetonitrile was removed *in vacuo*, and the red reside was dissolved in the minimum amount of pentane (~ 5 mL) and then eluted through a short plug of alumina (activity IV). The ruby red pentane solution was cooled to -34 °C, and **173** (16.1 mg, 0.0341 mmol, 71%) was harvested as a deep red crystalline solid. IR (microscope, cm^{-1}) 2998 (m), 2950 (m), 2904 (m), 2859 (m), 1749 (w), 1723 (s), 1454 (w), 1423 (w), 1374 (w), 1338 (w), 1283 (w), 1249 (m), 1221 (m), 1208 (m), 1130 (m), 1097 (w), 1066 (w), 1021 (w), 980 (w), 948 (w), 923 (w), 912 (w), 844 (w), 832 (w), 795 (w), 769 (w), 674 (w); ^{1}H NMR (500 MHz, C_6D_6) δ 4.17 (ddm, 1H, J_{H2-H3} = 7.2 Hz, J_{H3-H4} = 4.7 Hz, H_3), 3.91 (dd, 1H, J_{H3-H4} = 4.7 Hz, J_{H4-H5} = 6.3 Hz, H_4), 3.46 (s, 3H,-OC$\underline{H}_3$), 3.37 (s, 3H,-

$\mathrm{OC\underline{H}_3}$), 3.24 (d, 1H, $J_{\mathrm{H2\text{-}H3}}$ = 7.2 Hz, $\mathrm{H_2}$), 2.28 (td, 1H, $J_{\mathrm{H9(a\ or\ b)\text{-}H10a}} = J_{\mathrm{H10a\text{-}H10b}}$ = 14.2 Hz, $J_{\mathrm{H9(a\ or\ b)\text{-}H10a}}$ = 4.4 Hz, $\mathrm{H_{10a}}$), 2.19 (dm, 1H, $J_{\mathrm{H10a\text{-}H10b}}$ = 14.2 Hz, $\mathrm{H_{10b}}$), 2.12 (t, 1H, $J_{\mathrm{H4\text{-}H5}} = J_{\mathrm{H5\text{-}H6b}}$ = 6.3 Hz, $\mathrm{H_5}$), 1.67 (s, 15H, $\mathrm{C_5\underline{Me}_5}$), 1.65 (m, 1H, $J_{\mathrm{H7\text{-}H8a}}$ = 13.0 Hz, $\mathrm{H_7}$), 1.58 (m, 1H, $\mathrm{H_{9a}}$), 1.37 (m, 1H, $\mathrm{H_{9b}}$), 1.33 (m, 1H, $\mathrm{H_{6a}}$), 1.27 (s, 3H, $\mathrm{C_1\text{-}\underline{Me}}$), 1.18 (dddm, 1H, $J_{\mathrm{H5\text{-}H6b}}$ = 6.3 Hz, $J_{\mathrm{H6a\text{-}H6b}}$ = 16.6 Hz, $J_{\mathrm{H6b\text{-}H7}}$ = 3.7 Hz, $\mathrm{H_{6b}}$), 1.06 (app. qd, 1H, $J_{\mathrm{H7\text{-}H8a}} = J_{\mathrm{H8a\text{-}H8b}} = J_{\mathrm{H8a\text{-}H9(a\ or\ b)}}$ = 13.0 Hz, $J_{\mathrm{H8a\text{-}H9(a\ or\ b)}}$ = 4.2 Hz, $\mathrm{H_{8a}}$), 0.93 (br. d, 1H, $J_{\mathrm{H8a\text{-}H8b}}$ = 13.0 Hz, $\mathrm{H_{8b}}$); ^{1}H-^{1}H GCOSY (500 MHz, $\mathrm{C_6D_6}$) δ 4.17 ↔ δ 3.91, δ 3.24; δ 3.91 ↔ δ 2.12; δ 3.24 ↔ δ 1.27; δ 2.28 ↔ δ 2.19, δ 1.58, δ 1.37, δ 0.93; δ 2.19 ↔ δ 1.58, δ 1.37; δ 2.12 ↔ δ 1.33, δ 1.18; δ 1.65 ↔ δ 1.33, δ 1.18, δ 1.06, δ 0.93; δ 1.59 ↔ δ 1.37, δ 1.06, δ 0.93; δ 1.37 ↔ δ 1.06, δ 0.93; δ 1.33 ↔ δ 1.88; δ 1.06 ↔ δ 0.93; ^{13}C NMR (125 MHz, $\mathrm{C_6D_6}$) δ 172.1 ($\mathrm{\text{-}\underline{C}O_2CH_3}$), 171.2 ($\mathrm{\text{-}\underline{C}O_2CH_3}$), 89.8 ($\mathrm{\underline{C}_5Me_5}$), 83.1 ($\mathrm{C_3}$), 81.8 ($\mathrm{\underline{C}_4}$), 62.8 ($\mathrm{C_{11}}$), 59.2 ($\mathrm{C_2}$), 51.3 ($\mathrm{C_5}$ or $\mathrm{\text{-}O\underline{C}H_3}$), 51.2 ($\mathrm{C_5}$ or $\mathrm{\text{-}O\underline{C}H_3}$), 51.1 ($\mathrm{C_5}$ or $\mathrm{\text{-}O\underline{C}H_3}$), 43.1 ($\mathrm{C_1}$), 35.4 ($\mathrm{C_7}$), 33.3 ($\mathrm{C_6}$), 32.1 ($\mathrm{C_{10}}$), 29.2 ($\mathrm{C_8}$), 22.2 ($\mathrm{C_9}$), 18.9 ($\mathrm{C_1\text{-}\underline{Me}}$), 10.0 ($\mathrm{C_5\underline{Me}_5}$); HMQC (500 MHz, $\mathrm{C_6D_6}$) δ 83.1 ↔ δ 4.17; δ 81.8 ↔ δ 3.91; δ 59.2 ↔ δ 3.24; δ 51.3 ↔ δ 3.46 or δ 3.37 or δ 2.12; δ 51.2 ↔ δ 3.46 or δ 3.37 or δ 2.12; δ 51.1 ↔ δ 3.46 or δ 3.37 or δ 2.12; δ 35.4 ↔ δ 1.65; δ 33.3 ↔ δ 1.33, δ 1.18; δ 32.1 ↔ δ 2.28, δ 2.19; δ 29.2 ↔ δ 1.06, δ 0.93; δ 22.2 ↔ δ 1.58, δ 1.37; δ 18.9 ↔ δ 1.27; δ 10.0 ↔ δ 1.67. Analysis calculated for $\mathrm{C_{26}H_{37}CoO_4}$: C, 66.09; H, 7.89; found: C, 67.07; H, 8.12.



172 **180**

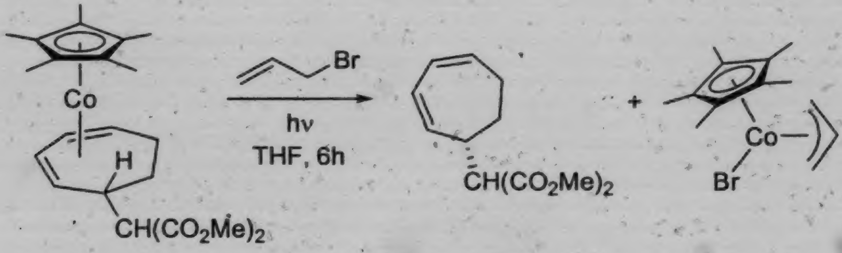
Oxidative decomplexation of 172: In the glove box, a small bomb was charged with a solution of Cp*Co(I) diene complex **172** (5.3 mg, 0.012 mmol) in THF (3 mL) and a small magnetic stir-bar. The bomb was removed to the Schlenk line where allyl bromide (5.0 μL, 0.058 mmol) was added via syringe. The mixture was then photolyzed using a Hanovia 450 W lamp for 7 hours, after which the solution was a pale blue-green and the solvent was removed *in vacuo*. The blue green residue was then chromatographed on silica gel (10% ether in hexanes) to furnish diene **180** (3.1 mg, 12 mmol, 100%) as a white solid upon drying. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, 1H, $J_{H2\text{-}H3}$ = 11.7 Hz, H_2), 5.78 (m, 1H, H_4), 5.69 (m, 2H, $J_{H2\text{-}H3}$ = 11.7 Hz, H_3 and H_5), 3.77 (3H, s, $-OCH_3$), 3.68 (3H, s, $-OCH_3$), 2.76 (m, 1H, H_7), 2.61 (m, 1H, H_{9a}), 2.43 (m, 1H, H_{6a}), 2.19 (m, 1H, H_{6b}), 2.08 (m, 1H, H_{9b}), 2.02 (m, 1H, H_{8a}), 1.34 (m, 1H, H_{8b}), 0.84 (s, 3H, C_1-Me); GCOSY (500 MHz, $CDCl_3$) δ 6.33 ↔ δ 5.69; δ 5.78 ↔ δ 5.69; δ 5.69 ↔ δ 2.43; δ 2.76 ↔ δ 2.43, δ 2.19, δ 2.02, δ 1.34; δ 2.61 ↔ δ 2.08, δ 2.02, δ 1.34; δ 2.43 ↔ δ 2.19; δ 2.08 ↔ δ 2.02, δ 1.34; δ 2.02 ↔ δ 1.34.



173 **181**

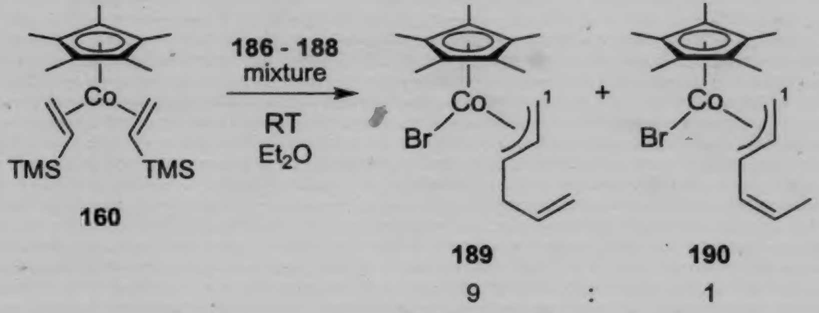
Oxidative decomplexation of 173: In the glove box, a small bomb reactor was charged with a solution of Cp*Co(I) diene complex **173** (17.3 mg, 0.0366 mmol) in THF (3 mL) and a small magnetic stir-bar. The bomb was removed to the Schlenk line where allyl bromide (20 μL, 0.22 mmol) was added via syringe. The mixture was then photolyzed using the Hanovia 450 W lamp for 12 hours, after which the solution was a pale blue-green and the solvent was removed *in vacuo*. The blue green residue was then chromatographed on silica gel (10% ether in hexanes) to furnish diene **181** (8.7 mg, 0.0312 mmol, 85%) as a white solid upon drying. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.27 (d, 1H, $J_{H2\text{-}H3}$ = 12.3 Hz, H$_2$), 5.75 (m, 2H, $J_{H2\text{-}H3}$ = 12.3 Hz, H$_3$ and H$_4$), 5.68 (ddd, 1H, $J_{H4\text{-}H5}$ = 12.3 Hz, $J_{H5\text{-}H6(a\text{ or }b)}$ = 6.6 Hz, $J_{H5\text{-}H6(a\text{ or }b)}$ = 1.1 Hz, H$_5$), 3.76 (3H, s, -OCH$_3$), 3.69 (3H, s, -OCH$_3$), 2.41 (m, 1H, H$_7$), 2.21 (m, 2H, H$_{6a}$ and H$_{6b}$), 2.08 (m, 2H, H$_{10}$), 1.67 (m, 1H, H$_{8a}$), 1.62 (m, 1H, H$_{9a}$), 1.15 (m, 2H, H$_{8b}$ and H$_{9b}$), 0.89 (s, 3H, C$_1$-Me); GCOSY (500 MHz, CDCl$_3$) δ 6.27 ↔ δ 5.68; δ 5.75 ↔ δ 5.68; δ 5.68 ↔ δ 2.21; δ 2.41 ↔ δ 2.21, δ 1.67, δ 1.15; δ 2.08 ↔ δ 1.62, δ 1.15; δ 1.67 ↔ δ 1.62, δ 1.15; δ 1.62 ↔ δ 1.15; ^{13}C NMR (125 MHz, CDCl$_3$) δ 172.0 (-$\underline{C}$O$_2$CH$_3$), 171.2 (-$\underline{C}$O$_2$CH$_3$), 140.1 (C$_3$ or C$_4$), 132.1

(C_3 or C_4), 123.9 (C_2 or C_5), 120.4 (C_2 or C_5), 64.0 (C_{11}), 52.3 (-O$\underline{C}H_3$), 52.0 (-O$\underline{C}H_3$), 44.4 (C_1), 37.1 (C_7 or C_{10}), 36.8 (C_7 or C_{10}), 31.2 (C_6), 29.3 (C_8), 21.6 (C_9), 18.9 (C_1-$\underline{Me}$).



182 **183** **184**

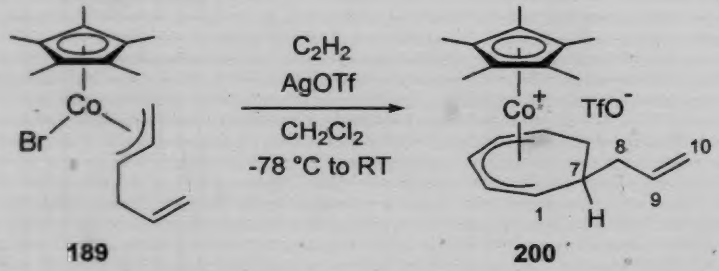
Oxidative decomplexation of 182 with recovery of 183 and 184: In the glove box, a glass bomb was charged with a solution of **182**[17] (81.1 mg, 0.194 mmol) in THF (2 mL). The bomb was removed to the Schlenk line, at which point allyl bromide (22 μL, 0.254 mmol) was injected via syringe. The bomb was sealed, and subjected to photolysis with the Hanovia 450W lamp for 6 hours. The irradiation was ceased, and purple solution was returned to the glove box. The solvent was removed *in vacuo* and the residue was redissolved in a minimal amount of THF. The resulting solution was then dripped into a flask containing pentane, at which point a dark blue-purple solid separated from the faintly purple supernatant. The supernatant was separated by filtration, concentrated, and removed from the box where chromatography on silica gel (15% ethyl acetate in hexanes) furnished clean **183** (36.1 mg, 0.161 mmol, 83%) upon solvent removal and drying. Complex **183** had been previously characterized by Dzwiniel.[17] In the glove box, the blue-purple filtrate was redissolved in diethyl ether and filtered through a plug of Celite to remove a small amount of blue-green solid. The purple solution was concentrated *in vacuo* and the residue was redissolved in a few drops of diethyl ether. The purple solution was then added to pentane (5 mL) and crystallization was allowed to proceed at -34 °C overnight. The next morning, Cp*Co(III) allyl bromide **184** (37.5 mg, 0.119 mmol, 61%) was recovered by vacuum filtration.



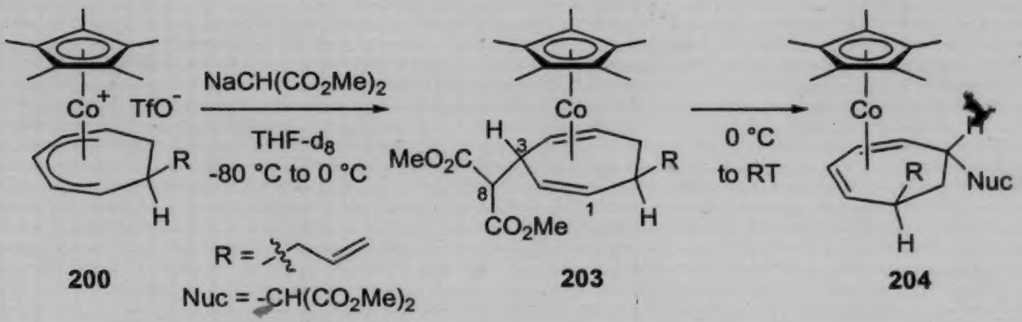
Cp*Co η^3-hexa-2,5-dien-1-yl bromide (189): A solution of CpCo(I) bis(vinyltrimethylsilane) **160** (2.1244 g, 5.3832 mmol) in diethyl ether (35 mL) was prepared in the glovebox and placed in a Schlenk flask equipped with a stir-bar and septum. The brick-red solution was removed to the Schlenk line and placed under an argon atmosphere. 3-Bromo-1,5-hexadiene (1.01 g, 6.27 mmol) was added via syringe and the resulting solution was stirred at room temperature for 20 minutes, after which the solvent was removed *in vacuo*. The purple residue was returned to the glovebox, redissolved in a small amount of ether, and filtered through Celite to remove a small amount of blue-green insoluble material. Upon removal of solvent, the crude **189** (1.7913 g, 5.0430 mmol, 94%) was suitable for further use, although crystals suitable for X-ray crystallography (1.6479 g, 4.6393 mmol, 86%) were grown from a mixture of diethyl ether and pentane cooled to -34 °C. A small amount (~ 10% by ^{1}H NMR integration) of

190 was also present, and the relative amount of this by-product was unaffected by the crystallization. For full crystallographic data, request report #JMS0344 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3072 (w), 3022 (m), 2972 (m), 2906 (m), 2842 (w), 1639 (m), 1557 (w), 1505 (m), 1480 (m), 1443 (m), 1416 (m), 1372 (s), 1271 (m), 1238 (w), 1199 (w), 1181 (m), 1161 (w), 1121 (w), 1071 (w), 1024 (s), 1009 (m), 981 (m), 936 (s), 917 (m), 880 (m), 835 (w), 740 (w); ^{1}H NMR (**189**, 500 MHz, C_6D_6) δ 5.97 (ddt, 1H, $J_{\text{H5-H6\textit{trans}}}$ = 17.1 Hz, $J_{\text{H5-H6\textit{cis}}}$ = 10.3 Hz, $J_{\text{H4a-H5}}$ = $J_{\text{H4b-H5}}$ = 5.8 Hz, H_5), 5.41 (dq, 1H, $J_{\text{H5-H6\textit{trans}}}$ = 17.1 Hz, $J_{\text{H4a-H6\textit{trans}}}$ = $J_{\text{H4b-H6\textit{trans}}}$ = $J_{\text{H6\textit{cis}-H6\textit{trans}}}$ = 1.8 Hz, $H_{6\textit{trans}}$), 5.09 (dq, 1H, $J_{\text{H5-H6\textit{cis}}}$ = 10.3 Hz, $J_{\text{H4a-H6\textit{cis}}}$ = $J_{\text{H4b-H6\textit{cis}}}$ = $J_{\text{H6\textit{cis}-H6\textit{trans}}}$ = 1.8 Hz, $H_{6\textit{cis}}$), 3.71 (m, 1H, $J_{\text{H2-H3}}$ = 12.2 Hz, H_3), 3.59 (d, 1H, $J_{\text{H1\textit{syn}-H2}}$ = 7.4 Hz, $H_{1\textit{syn}}$), 3.42 (td, 1H, $J_{\text{H1\textit{anti}-H2}}$ = $J_{\text{H2-H3}}$ = 12.2 Hz, $J_{\text{H1\textit{syn}-H2}}$ = 7.4 Hz, H_2), 3.25 (d, 1H, $J_{\text{H1\textit{anti}-H2}}$ = 12.2 Hz, $H_{1\textit{anti}}$), 2.63 (m, 1H, $J_{\text{H4a-H6trans}}$ = $J_{\text{H4a-H6cis}}$ = 1.8 Hz, $J_{\text{H4a-H5}}$ = 5.8 Hz, H_{4a}), 2.20 (m, 1H, $J_{\text{H4b-H6trans}}$ = $J_{\text{H4b-H6cis}}$ = 1.8 Hz, $J_{\text{H4b-H5}}$ = 5.8 Hz, H_{4b}), 1.27 (s, 15H, $CpMe_5$); ^{1}H-^{1}H GCOSY (**189**, 500 MHz, C_6D_6) δ 5.97 ↔ δ 5.41, δ 5.09, δ 2.63, δ 2.20; δ 5.41 ↔ δ 5.09, δ 2.63, δ 2.20; δ 5.09 ↔ δ 2.63, δ 2.20; δ 3.71 ↔ δ 3.42, δ 3.25, δ 2.63, δ 2.20; δ 3.59 ↔ δ 3.42, δ 3.25; δ 3.42 ↔ δ 3.25; δ 2.63 ↔ δ 2.20; ^{13}C NMR (**189**, 100 MHz, C_6D_6) δ 136.6 (C_5), 115.6 (C_6), 95.7 (C_3), 93.2 ($\underline{C_5}Me_5$), 74.2 (C_2), 54.6 (C_1), 37.4 (C_4), 10.0 ($C_5\underline{Me_5}$). ^{1}H NMR (**190**, 500 MHz, C_6D_6) δ 6.22 (dqd, 1H, $J_{\text{H4-H5}}$ = 10.5 Hz, $J_{\text{H5-H6}}$ = 7.2 Hz, $J_{\text{H3-H5}}$ = 1.3 Hz, H_5), 5.46 (app. tq, 1H, $J_{\text{H3-H4}}$ = $J_{\text{H4-H5}}$ = 10.5 Hz, $J_{\text{H4-H6}}$ = 1.8 Hz, H_4), 4.53 (app. t, 1H, $J_{\text{H3-H4}}$ = 10.5 Hz, $J_{\text{H2-H3}}$ = 12.1 Hz, H_3), 3.73 (d, 1H, $J_{\text{H1syn-H2}}$ = 7.7 Hz, $H_{1\text{syn}}$), 3.64 (dt, 1H, $J_{\text{H1syn-H2}}$ = 7.7 Hz, $J_{\text{H1anti-H2}}$ = $J_{\text{H2-H3}}$ = 12.1 Hz, H_2), 3.43 (d, 1H, $J_{\text{H1anti-H2}}$ = 12.1 Hz, $H_{1\text{anti}}$), 1.53 (dd, 3H, $J_{\text{H4-H6}}$ = 1.8 Hz, $J_{\text{H5-H6}}$ = 7.2 Hz, H_6), 1.23 (s, 15H, $CpMe_5$); ^{1}H-^{1}H GCOSY (**190**, 500 MHz, C_6D_6) δ 6.22 ↔ δ

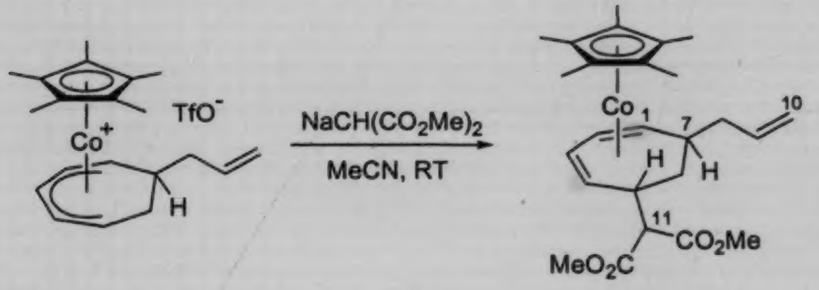
5.46, δ 4.53, δ 1.53; δ 5.46 ↔ δ 4.53, δ 1.53; δ 4.53 ↔ δ 3.64, δ 3.43. Correlations of peaks at δ 3.73, δ 3.64, and δ 3.43 are obscured by those of the major compound, **189**. ^{13}C NMR (**190**, 100 MHz, C_6D_6) δ 132.8 (C_4), 127.9 (C_5), 95.9 ($\underline{C_5}Me_5$), 92.6 (C_2), 73.0 (C_3), 54.5 (C_1), 15.5 (C_6), 9.7 ($C_5\underline{Me_5}$).



Cp*Co(III) 7-Allyl-cycloheptadienyl trifluoromethanesulfonate (200): In the glove box, a 25mL round-bottom flask was charged with silver triflate (209.0 mg, 0.8134 mmol) and equipped with a stir-bar and septum. As well, a vial was charged with Cp*Co(III) allyl complex **189** (276.4 mg, 0.7781 mmol) and fitted with a rubber septum. Both containers were removed to the Schlenk line and placed under an argon atmosphere. Complex **189** was dissolved in degassed dichloromethane (5 mL) and the silver triflate was suspended in dichloromethane (20 mL), and both mixtures were cooled to -78 °C. Acetylene was streamed into the silver triflate suspension for a minute, and the purple solution of **189** was then transferred, via cannula, into the suspension. The acetylene stream was resumed for an additional 3 minutes, and the reaction was allowed to stir at -78 °C for 15 minutes. The cooling bath was then removed, and the reaction was stirred at room temperature for 19 hours. The solvent was removed *in vacuo*, and the red-brown residue was chromatographed twice on silica gel (once with 2% MeOH in CH_2Cl_2, once with 4% MeOH in CH_2Cl_2) and, upon drying, **200** (282.3 mg, 0.5925 mmol, 76%) was obtained as an orange-red solid. IR (microscope, cm^{-1}) 3060 (m), 2988 (m), 2911 (m), 2293 (w), 1641 (m), 1470 (m), 1407 (w), 1387 (m), 1262 (s), 1224 (m), 1154 (s), 1076 (m), 1031 (m), 994 (m), 914 (m), 882 (m), 812 (w), 753 (m), 734 (m), 701 (m), 638 (s), 572 (m), 517 (s), 495 (m), 418 (s); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.58 (app. tm, 1H, J_{H2-H3} = 6.3 Hz, J_{H3-H4} = 7.1 Hz, H_3), 5.66 (ddt, $J_{H9-H10cis}$ = 10.7 Hz, $J_{H9-H10trans}$ = 17.5 Hz, J_{H8-H9} = 6.9 Hz, H_9), 5.23 (ddm, 1H, J_{H1-H2} = 8.1 Hz, J_{H2-H3} = 6.3 Hz, H_2), 5.08 (2H, m, $J_{H9-H10cis}$ = 10.7 Hz, $J_{H9-H10trans}$ = 17.5 Hz, H_{10cis} and $H_{10trans}$), 4.88 (ddm, 1H, J_{H3-H4} = 7.1 Hz, J_{H4-H5} = 9.3 Hz, H_4), 4.33 (ddd, 1H, J_{H4-H5} = 9.3 Hz, J_{H5-H6a} = 4.4 Hz, J_{H5-H6b} = 3.3 Hz, H_5), 4.09 (ddm, 1H, J_{H1-H2} = 8.1 Hz, J_{H1-H7} = 4.1 Hz, H_1), 2.47 (ddd, 1H, J_{H5-H6a} = 4.4 Hz, $J_{H6a-H6b}$ = 16.8 Hz, J_{H6a-H7} = 9.7 Hz, H_{6a}), 2.14 (m, 2H, H_8), 2.07 (dddd, 1H, J_{H5-H6b} = 3.3 Hz, $J_{H6a-H6b}$ = 16.8 Hz, J_{H6b-H7} = 5.5 Hz, $J_{H6b-(H4\ or\ H1)}$ = 1.5 Hz, H_{6b}), 1.87 (s, 15H, $C_5\underline{Me}_5$), 0.79 (m, 1H, J_{H6a-H7} = 9.7 Hz, J_{H6b-H7} = 5.5 Hz, H_7); ^{1}H-^{1}H GCOSY (400 MHz, CD_2Cl_2) δ 6.58 ↔ δ 5.23, δ 4.88, δ 4.09; δ 5.66 ↔ δ 5.08, δ 2.14; δ 5.23 ↔ δ 4.09; δ 5.08 ↔ δ 2.14; δ 4.88 ↔ δ 4.33, δ 2.07; δ 4.33 ↔ δ 2.47, δ 2.07; δ 4.09 ↔ δ 0.79; δ 2.47 ↔ δ 2.07, δ 0.79; δ 2.14 ↔ δ 0.79; δ 2.07 ↔ δ 0.79; ^{13}C NMR (125 MHz, CD_2Cl_2) δ 135.5 (C_9), 117.8 (C_{10}), 100.6 (C_3), 99.3 ($\underline{C}_5Me_5$), 98.1 (C_2), 97.9 (C_4), 94.3 (C_1), 89.2 (C_5), 46.7 (C_6), 40.0 (C_8), 39.5 (C_7), 10.0 ($C_5\underline{Me}_5$). HMQC (500 MHz, CD_2Cl_2) δ 135.5 ↔ δ 5.66; δ 117.8 ↔ δ 5.08; δ 100.6 ↔ δ 6.58; δ 98.1 ↔ δ 5.23; δ 97.9 ↔ δ 4.88; δ 94.3 ↔ δ 4.09; δ 89.2 ↔ δ 4.33; δ 46.7 ↔ δ 2.47, δ 2.07; δ 40.0 ↔ δ 2.14; δ 39.5 ↔ δ 0.79; δ 10.0 ↔ δ 1.87. Analysis calculated for $C_{21}H_{28}CoF_3O_3S$: C, 52.94; H, 5.92; found: C, 52.81; H, 6.04.



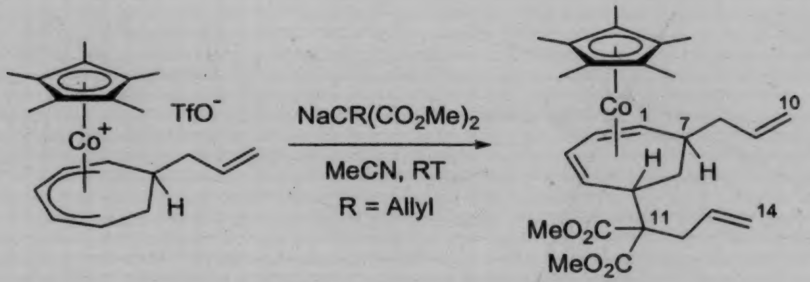
Variable-temperature NMR study of the regioselectivity of malonate addition to 200: A suspension of the sodium salt of dimethyl malonate (4.0 mg, 0.026 mmol) in THF-d$_8$ (350 μL) was prepared in an NMR tube in the glove box, and the tube was fitted with a rubber septum. Likewise, a solution of complex **200** (12.5 mg, 0.0263 mmol) in THF-d$_8$ (350 μL) was prepared in a small vial, which was fitted with a rubber septum. Both solutions were removed to the fume hood and cooled to -78 °C, at which point the solution of **200** was transferred via cannula into the NMR tube. The NMR tube was quickly transferred to the spectrometer (400 MHz) which had been pre-cooled to -80 °C. NMR interrogation of the sample was performed at 20 °C intervals as the tube was warmed to room temperature over a period of several hours. At -80 °C, only starting materials could be detected, and ^{1}H NMR integration revealed that an excess of **200** was present, likely due to weighing error in the amount of nucleophile added. ^{1}H NMR signals (ascribed to intermediate complex **203**) at δ 3.80 (m, H$_3$) and δ 3.24 (d, $J_{H3\text{-}H8}$ = 11.6 Hz, H$_8$) were visible between -60 °C and -20 °C; other resonances attributable to **203** were obscured by signals arising from starting material **200**. Above 0 °C, the signals arising from **203** were replaced by signals corresponding to terminal adduct **204**, which was independently synthesized and characterized as described below.



200 **204**

Cp*Co(I) η^4-(dimethyl (6-allylcyclohepta-2,4-dien-1-yl)malonate) (204): In the glove box, a solution of cycloheptadienyl complex **200** (142.3 mg, 0.2987 mmol) in acetonitrile (4 mL) was prepared and subsequently charged with sodium salt of dimethyl malonate (47.3 mg, 0.307 mmol). The resulting red solution was maintained at room temperature for 30 minutes, and then the solvent was removed *in vacuo*. The red residue was taken up in pentane (5 mL) and then filtered, with rinsing, through Celite. Upon removal of pentane *in vacuo* crude **204** was recovered as a ruby red solid (128.4 mg, 0.2801 mmol, 94%) which was very clean by ^{1}H NMR. The crude product was crystallized at -34 °C from pentane to furnish analytically pure **204** (107.6 mg, 0.2347 mmol, 79%) as ruby-red crystals suitable for X-ray crystallography. For full crystallographic data, request report #JMS0406 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3456 (w), 3079 (w), 2990 (s), 2935 (s), 2909 (s), 2853 (s), 2820 (m), 2730 (w), 1754 (s), 1732 (s), 1643 (w), 1490 (m), 1437 (s), 1377 (s), 1316 (s), 1300 (s), 1259 (s), 1248 (s), 1235 (s), 1211 (s), 1164 (s), 1143 (s), 1111 (m), 1071 (w), 1051 (m), 1030 (m), 1016 (m), 994 (m), 968 (w), 956 (m), 929 (m), 906 (m), 847 (m), 827 (m), 803 (w), 710 (w), 670(w); ^{1}H NMR (500 MHz, C_6D_6) δ 5.87 (m, 1H, $J_{H9-H10cis}$ = 10.2 Hz , $J_{H9-H10trans}$ = 17.1

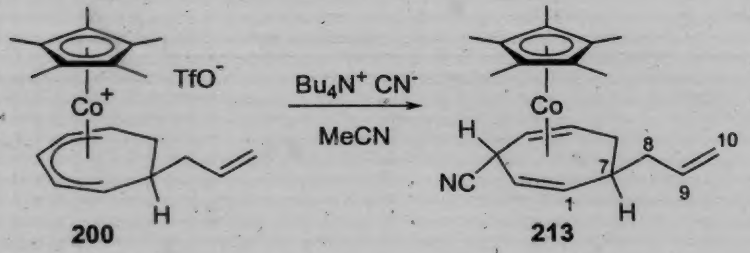
Hz, H_9), 5.19 (dm, 1H, $J_{H9\text{-}H10trans}$ = 17.1 Hz, $H_{10trans}$), 5.05 (dm, 1H, $J_{H9\text{-}H10cis}$ = 10.2 Hz, H_{10cis}), 3.99 (ddm, 1H, $J_{H1\text{-}H2}$ = 7.0 Hz, $J_{H2\text{-}H3}$ = 4.7 Hz, H_2), 3.84 (ddd, 1H, $J_{H2\text{-}H3}$ = 4.7 Hz, $J_{H3\text{-}H4}$ = 7.0 Hz, $J_{H3\text{-}H5}$ = 0.8 Hz, H_3), 3.37 (s, 3H, $-OCH_3$), 3.29 (s, 3H, $-OCH_3$), 3.25 (d, 1H, $J_{H5\text{-}H11}$ = 8.8 Hz, H_{11}), 2.59 (m, 1H, $J_{H5\text{-}H11}$ = 8.8 Hz, H_5), 2.31 (m, 2H, H_8), 2.20 (dm, 1H, $J_{H3\text{-}H4}$ = 7.0 Hz, H_4), 2.15 (ddm, 1H, $J_{H1\text{-}H2}$ = 7.0 Hz, $J_{H1\text{-}H7}$ = 5.1 Hz, H_1), 1.66 (s, 15H, $CpMe_5$), 1.48 (m, 1H, $J_{H1\text{-}H7}$ = 5.1, H_7), 1.25 (dm, 1H, $J_{H6a\text{-}H6b}$ = 13.0 Hz, H_{6a}), 0.81 (td, 1H, $J_{H5\text{-}H6b}$ = $J_{H6a\text{-}H6b}$ = 13.0 Hz, $J_{H6b\text{-}H7}$ = 4.4 Hz, H_{6b}); $^1H\text{-}^1H$ GCOSY (500 MHz, C_6D_6) δ 5.87 ↔ δ 5.19, δ 5.05, δ 2.31; δ 5.19 ↔ δ 5.05, δ 2.31; δ 5.05 ↔ δ 2.31; δ 3.99 ↔ δ 3.84, δ 2.15; δ 3.84 ↔ δ 2.20; δ 3.25 ↔ δ 2.59; δ 2.59 ↔ δ 2.20, δ 1.25, δ 0.81; δ 2.31 ↔ δ 1.48; δ 2.20 ↔ δ 1.25; δ 2.15 ↔ δ 1.48, δ 1.25; δ 1.48 ↔ δ 1.25, δ 0.81; δ 1.25 ↔ δ 0.81; ^{13}C NMR (C_6D_6, 125 MHz) δ 169.2 ($-\underline{C}O_2CH_3$), 168.6 ($-\underline{C}O_2CH_3$), 138.6 (C_9), 115.7 (C_{10}), 90.2 ($\underline{C}_5Me_5$), 82.2 (C_2), 80.8 (C_3), 60.2 (C_{11}), 58.1 (C_1), 54.0 (C_4), 51.6 ($-OCH_3$), 51.5 ($-OCH_3$), 39.7 (C_8), 36.8 (C_6), 33.6 (2 peaks, C_5 and C_7), 10.0 ($C_5\underline{Me}_5$); HMQC (500 MHz, C_6D_6) δ 138.6 ↔ δ 5.87; δ 115.7 ↔ δ 5.19, δ 5.05; δ 82.2 ↔ δ 3.99; δ 80.8 ↔ δ 3.84; δ 60.2 ↔ δ 3.25; δ 58.1 ↔ δ 2.15; δ 54.0 ↔ δ 2.20; δ 51.6 ↔ δ 3.37; δ 51.5 ↔ δ 3.29; δ 39.7 ↔ δ 2.31; δ 36.8 ↔ δ 1.25, δ 0.81; δ 33.6 ↔ δ 2.58, δ 1.48; δ 10.0 ↔ δ 1.66. Analysis calculated for $C_{25}H_{35}CoO_4$: C, 65.49; H, 7.69; found: C, 65.48; H, 7.78.



200 **205**

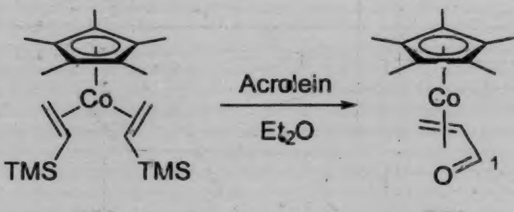
Cp*Co(I) η⁴-(dimethyl allyl(6-allylcyclohepta-2,4-dien-1-yl)malonate) (205): In the glove box, a vial was charged with a solution of cycloheptadienyl complex **200** (102.3 mg, 0.2147 mmol) in acetonitrile (10 mL). Solid sodium salt of dimethyl allylmalonate (42.0 mg, 0.2163 mmol) was added, and the resulting mixture was stirred at room temperature for 30 minutes, after which the solvent was removed *in vacuo*. The red residue was taken up in hexane (3 mL) and filtered through Celite. Removal of solvent and subsequent drying under vacuum afforded crude **205** (107.6 mg, 0.2158 mmol, 100%) as a red solid, which was recrystallized from pentane (1 mL) at -34 °C to furnish **205** (71.9 mg, 0.1442 mmol, 67%) as a red crystalline solid. For full crystallographic data, request report #JMS0325 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3059 (w), 3018 (w), 3002 (w), 2967 (m), 2952 (m), 2913 (m), 2859 (w), 2720 (w), 1847 (w), 1728 (s), 1639 (m), 1546 (w), 1491 (w), 1447 (m), 1438 (m), 1428 (m), 1373 (m), 1338 (m), 1308 (m), 1297 (m), 1260 (m), 1211 (s), 1183 (m), 1132 (m), 1096 (w), 1067 (m), 1035 (m), 1014 (m), 1005 (m), 954 (w), 920 (m), 875 (m), 863 (w), 832 (m), 821 (w), 668 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 6.13 (ddt, 1H, $J_{H13\text{-}H14cis}$ = 10.1 Hz, $J_{H13\text{-}H14trans}$ = 17.2 Hz, $J_{H12\text{-}H13}$ = 7.2 Hz, H_{13}), 5.88 (m, 1H, $J_{H9\text{-}H10cis}$ = 10.1 Hz , $J_{H9\text{-}H10trans}$ =

17.2 Hz , H_9), 5.17 (dm, 1H, $J_{H9\text{-}H10trans}$ = 17.2 Hz, $H_{10trans}$), 5.09 (dm, 1H, $J_{H13\text{-}H14trans}$ = 17.2 Hz, $H_{14trans}$), 5.03 (dm, 1H, $J_{H9\text{-}H10cis}$ = 10.1 Hz, H_{10cis}), 5.01 (dm, 1H, $J_{H13\text{-}H14cis}$ = 10.1 Hz, H_{14cis}), 3.97 (ddm, 1H, $J_{H1\text{-}H2}$ = 6.6 Hz, $J_{H2\text{-}H3}$ = 4.6 Hz, H_2), 3.91 (ddd, 1H, $J_{H2\text{-}H3}$ = 4.6 Hz, $J_{H3\text{-}H4}$ = 7.0 Hz, H_3), 3.41 (s, 6H, -OCH_3), 2.84 (m, 2H, $J_{H12\text{-}H13}$ = 7.2 Hz, H_{12}), 2.44 (dm, 1H, $J_{H5\text{-}H6b}$ = 12.9 Hz, H_5), 2.32 (m, 3H, $J_{H3\text{-}H4}$ = 7.0 Hz, H_4 and H_8), 2.15 (ddm, 1H, $J_{H1\text{-}H2}$ = 6.6 Hz, $J_{H1\text{-}H7}$ = 5.5 Hz, H_1), 1.68 (s, 15H, $CpMe_5$), 1.60 (m, 1H, $J_{H1\text{-}H7}$ = 5.5 Hz, $J_{H6b\text{-}H7}$ = 4.4 Hz, H_7), 1.30 (d, 1H, $J_{H6a\text{-}H6b}$ = 12.9 Hz, H_{6a}), 0.73 (td, 1H, $J_{H5\text{-}H6b}$ = $J_{H6a\text{-}H6b}$ = 12.9 Hz, $J_{H6b\text{-}H7}$ = 4.4 Hz, H_{6b}); ^1H-^1H GCOSY (300 MHz, C_6D_6) δ 6.13 ↔ δ 5.09, δ 5.01, δ 2.84; δ 5.88 ↔ δ 5.17, δ 5.03, δ 2.32; δ 5.17 ↔ δ 5.03, δ 2.32; δ 5.09 ↔ δ 5.01, δ 2.84; δ 5.03 ↔ δ 2.32; δ 5.01 ↔ δ 2.84; δ 3.97 ↔ δ 3.91, δ 2.15; δ 3.91 ↔ δ 2.32; δ 2.44 ↔ δ 1.30, δ 0.73; δ 2.32 ↔ δ 1.60; δ 2.15 ↔ δ 1.60; δ 1.60 ↔ δ 1.30, δ 0.73; δ 1.30 ↔ δ 0.73; ^{13}C NMR (C_6D_6, 100 MHz) δ 138.6 (C_9), 135.2 (C_{13}), 117.4 (C_{14}), 115.3 (C_{10}), 90.0 ($\underline{C}_5Me_5$), 81.8 (C_2), 81.3 (C_3), 57.4 (C_1), 52.5 (C_4), 51.5 (-OCH_3), 51.0 (-OCH_3), 39.2 (C_8), 38.3 (C_5), 38.1 (C_{12}), 27.0 (C_6), 26.6 (C_7), 9.7 ($C_5\underline{Me}_5$); HMQC (300 MHz, C_6D_6) δ 138.6 ↔ δ 5.88; δ 135.2 ↔ δ 6.13; δ 117.4 ↔ δ 5.09, δ 5.01; δ 115.3 ↔ δ 5.17, δ 5.03; δ 81.8 ↔ δ 3.97; δ 81.3 ↔ δ 3.91; δ 57.4 ↔ δ 2.15; δ 52.5 ↔ δ 2.33; δ 51.5 ↔ δ 3.41; δ 51.0 ↔ δ 3.41; δ 39.2 ↔ δ 2.30; δ 38.3 ↔ δ 2.44; δ 38.1 ↔ δ 2.84; δ 27.0 ↔ δ 1.30, δ 0.73; δ 26.6 ↔ δ 1.60; δ 9.7 ↔ δ 1.68. Analysis calculated for $C_{28}H_{39}CoO_4$: C, 67.46; H, 7.89; found: C, 67.66; H, 7.91.



Cp*Co(I) η^4-4-cyano-1-allylcyclohepta-2,5-diene (213): In the glove box, a vial was charged with a solution of cycloheptadienyl complex **200** (188.6 mg, 0.3959 mmol) in acetonitrile (1 mL). A solution of tetrabutylammonium cyanide (120.1 mg, 0.4473 mmol) in acetonitrile (1 mL) was added, and the resulting mixture was stirred at room temperature for 10 minutes, after which the solvent was removed *in vacuo*. The yellow residue was taken up in a mixture of benzene (1 mL) and pentane (1 mL) and filtered through Celite. Removal of solvent and subsequent drying under vacuum afforded **213** (113.1 mg, 0.3200 mmol, 81%) as a yellow powder. IR (microscope, cm^{-1}) 3070 (m), 3005 (s), 2992 (s), 2972 (s), 2944 (s), 2906 (s), 2855 (s), 2219 (m), 1812 (w), 1637 (m), 1447 (s), 1384 (s), 1376 (s), 1363 (m), 1344 (m), 1318 (m), 1294 (m), 1232 (m), 1216 (m), 1182 (w), 1163 (w), 1086 (m), 1027 (m), 998 (m), 935 (w), 905 (s), 882 (w), 824 (w), 795 (w), 734 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 5.75 (ddt, 1H, $J_{H9\text{-}H10\mathit{cis}}$ = 10.2 Hz, $J_{H9\text{-}H10\mathit{trans}}$ = 17.1 Hz, $J_{H8\text{-}H9}$ = 6.9 Hz, H_9), 5.14 (dm, 1H, $J_{H9\text{-}H10\mathit{trans}}$ = 17.1 Hz, $H_{10\mathit{trans}}$), 5.05 (dm, 1H, $J_{H9\text{-}H10\mathit{cis}}$ = 10.2 Hz, $H_{10\mathit{cis}}$), 3.54 (t, 1H, $J_{H2\text{-}H3}$ = $J_{H3\text{-}H4}$ = 7.9 Hz, H_3), 2.55 (m, 1H, $J_{H2\text{-}H7}$ = 1.7 Hz, $J_{H6a\text{-}H7}$ = 7.9 Hz, $J_{H6b\text{-}H7}$ = 5.1 Hz, H_7), 2.47 (dd, 1H, $J_{H6a\text{-}H6b}$ = 14.8 Hz, $J_{H6a\text{-}H7}$ = 7.9 Hz, H_{6a}), 2.31 (m, 2H, $J_{H8\text{-}H9}$ = 6.9 Hz, H_8), 1.91 (ddd, 1H, $J_{H6a\text{-}H6b}$ = 14.8 Hz, $J_{H6b\text{-}H7}$ = 5.1 Hz, $J_{H5\text{-}H6b}$ = 7.5 Hz, H_{6b}), 1.76 (dd, 1H, $J_{H1\text{-}H2}$ = 7.5 Hz, $J_{H2\text{-}H7}$ = 1.7 Hz, H_2), 1.71 (td, 1H, $J_{H4\text{-}H5}$ = $J_{H5\text{-}H6b}$ = 7.5 Hz, $J_{H5\text{-}H6a}$ = 1.7 Hz, H_5), 1.37 (s, 15H,

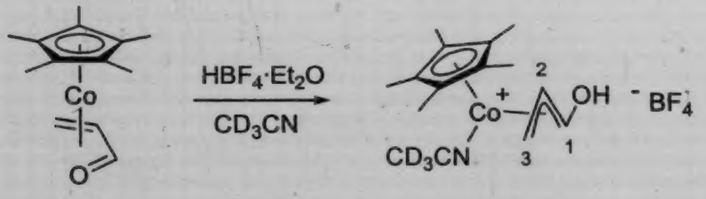
$CpMe_5$), 1.27 (app. t, 1H, $J_{H1\text{-}H2}$ = 7.5 Hz, $J_{H2\text{-}H3}$ = 7.9 Hz , H_2), 1.20 (app. t, 1H, $J_{H3\text{-}H4}$ = 7.9 Hz, $J_{H4\text{-}H5}$ = 7.5 Hz, H_4); ^1H-^1H GCOSY (400 MHz, C_6D_6) δ 5.75 ↔ δ 5.14, δ 5.05, δ 2.31; δ 5.14 ↔ δ 5.05, δ 2.31; δ 5.05 ↔ δ 2.31; δ 3.54 ↔ δ 1.27, δ 1.20; δ 2.55 ↔ δ 2.47, δ 2.31, δ 1.91, δ 1.76, δ 1.27; δ 2.47 ↔ δ 1.91, δ 1.71; δ 1.91 ↔ δ 1.71; δ 1.76 ↔ δ 1.27; δ 1.71 ↔ δ 1.20; ^{13}C NMR (125 MHz, C_6D_6) δ 138.3 (C_9), 118.1 (CN), 116.0 (C_{10}), 91.6 ($\underline{C}_5Me_5$), 72.0 (C_1 or C_5), 65.6 (C_1 or C_5), 44.2 (C_2 or C_4), 40.0 (C_2 or C_4), 37.5 (C_8), 27.2 (C_3, C_6, or C_7), 26.8 (C_3, C_6, or C_7), 26.6 (C_3, C_6, or C_7), 9.5 ($C_5\underline{Me}_5$). Analysis calculated for $C_{21}H_{28}CoN$: C, 71.37; H, 7.99; found: C, 71.34; H, 8.16.



160 **241**

Cp*Co(I) (η^4-acrolein) (241): In a Schlenk flask equipped with a stir-bar and rubber septum, Cp*Co bis(vinyltrimethylsilane) **160** (237.6 mg, 0.6021 mmol) was dissolved in diethyl ether (10 mL) in the glove box and removed to the Schlenk line. Under an inert atmosphere, freshly distilled acrolein (800 µL, 1.20 mmol) was added by syringe, and the solution changed rapidly in colour from a deep red-brown to an olive green. After stirring at room temperature for 20 minutes, the solvent was removed *in vacuo* and the residue was returned to the glove box. The residue was dissolved in pentane, and filtered through a Celite plug. Crystallization was induced by cooling the solution to -80 °C, and green crystalline **241** (129.1 mg, 0.5160 mmol, 86%) was obtained after cannula-removal of the supernatant solution and subsequent drying under vacuum. Although ^{1}H NMR revealed that **241** was obtained in high purity, the high air-sensitivity of **241** precluded elemental analysis within 0.4% of calculated values; the best of several runs is reported below. IR (microscope, cm^{-1}) 3062 (m), 3048 (m), 2976 (s), 2952 (s), 2907 (s), 2860 (m), 2761 (w), 2459 (w), 2400 (w), 1840 (w), 1756 (w), 1449 (m), 1408 (s), 1376 (m), 1235 (s), 1165 (m), 1072 (m), 1042 (m), 1028 (m), 997 (m), 949 (w), 921 (w), 895 (w), 879 (w), 797 (w), 748 (w), 718 (m);^{1}H NMR (400 MHz, C_6D_6) δ

7.28 (d, 1H, $J_{H1\text{-}H2}$ = 0.6 Hz, H_1), 4.27 (ddd, 1H, $J_{H1\text{-}H2}$ = 0.6 Hz, $J_{H2\text{-}H3anti}$ = 9.7 Hz, $J_{H2\text{-}H3syn}$ = 6.4 Hz, H_2), 1.63 (br d, 1H, $J_{H2\text{-}H3syn}$ = 6.4 Hz, H_{3syn}), 1.56 (s, 15H, $CpMe_5$), 1.34 (dd, 1H, $J_{H2\text{-}H3anti}$ = 9.7 Hz, $J_{H3syn\text{-}H3anti}$ = 0.9 Hz, H_{3syn}); ^{1}H-^{1}H GCOSY (400 MHz, C_6D_6) δ 7.28 ↔ δ 4.27, δ 1.63, δ 1.34; δ 4.27 ↔ δ 1.63, δ 1.34; ^{13}C NMR (100 MHz, C_6D_6) δ 122.2 (C_1), 89.6 ($\underline{C_5}Me_5$), 80.5 (C_2), 37.0 (C_3), 10.0 ($C_5\underline{Me_5}$); HMQC (400 MHz, C_6D_6) δ 122.2 ↔ δ 7.28; δ 80.5 ↔ δ 4.27; δ 37.0 ↔ δ 1.63, δ 1.34; δ 10.0 ↔ δ 1.56. Analysis calculated for $C_{13}H_{19}CoO$: C, 62.40; H, 7.65; found: C, 61.37; H, 7.70.

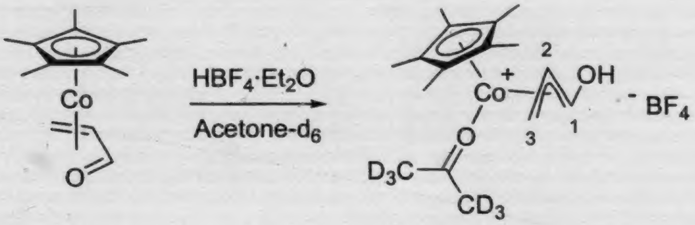


241 **245**

Cp*Co(III) (η^3-hydroxyallyl) acetonitrile complex in-tube observation (245): In the glove box, an NMR tube was charged with a solution of **241** (12.2 mg, 0.0488 mmol) in MeCN-d_3 (~ 600 µl), and fitted with a rubber septum. The tube was removed from the drybox, and a solution of HBF_4 (54% in Et_2O, 7.0 µL, 0.051 mmol) was added via syringe. The sample was inverted several times, and the solution immediately turned brown. Complex **245** was characterized by ^{1}H NMR spectroscopy only, and was not isolated. ^{1}H NMR (300 MHz, CD_3CN) δ 6.74 (d, 1H, $J_{H1\text{-}OH}$ = 6.1 Hz, -OH), 5.18 (dd, 1H, $J_{H1\text{-}OH}$ = 6.1 Hz, $J_{H1\text{-}H2}$ = 9.7 Hz, H_1), 3.92 (ddd, 1H, $J_{H1\text{-}H2}$ = 9.7 Hz, $J_{H2\text{-}H3syn}$ = 8.1 Hz, $J_{H2\text{-}H3anti}$ = 12.3 Hz, H_2), 3.56 (dd, 1H, $J_{H2\text{-}H3syn}$ = 8.1 Hz, $J_{H3syn\text{-}H3anti}$ = 1.0 Hz, H_{3syn}), 1.64 (dm, 1H, $J_{H2\text{-}H3anti}$ = 12.3 Hz, $J_{H3syn\text{-}H3anti}$ = 1.0 Hz, H_{3anti}), 1.55 (s, 15H, $CpMe_5$); ^{1}H-

^{1}H GCOSY (300 MHz, CD_3CN) δ 6.74 ↔ δ 5.18; δ 5.18 ↔ δ 3.92; δ 3.92 ↔ δ 3.56, δ 1.64; δ 3.56 ↔ δ 1.64.

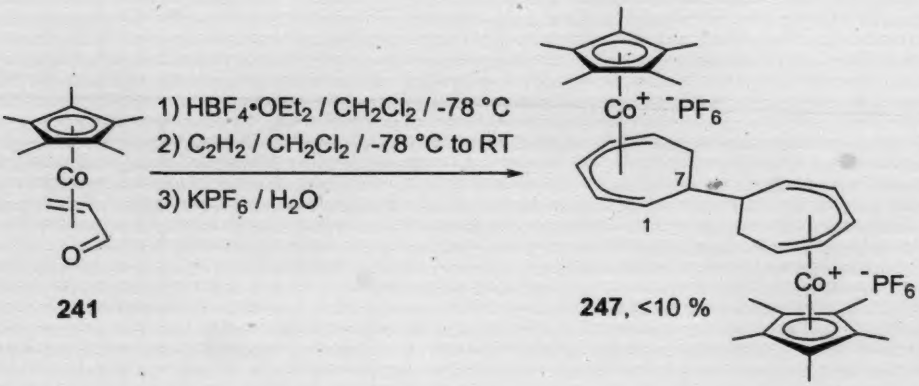
The reactivity of **245** with acetylene was subsequently probed; acetylene gas was gently streamed via a long needle through the solution. During this streaming, the septum was fitted with a narrow gauge needle to allow excess gas to vent. Acetylene was streamed in this manner for several minutes, and the resulting solution was allowed to stand at room temperature for 30 minutes. Excess acetylene was then removed under a slow stream of argon, prior to NMR analysis which revealed no evidence for seven-membered rings.



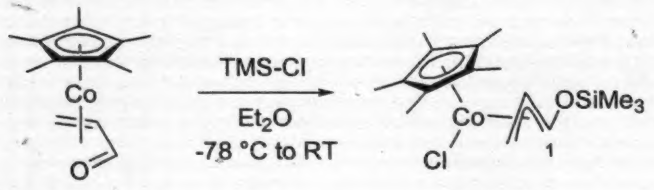
241 **246**

Cp*Co(III) (η^3-hydroxyallyl) acetone complex in-tube observation (246): In the glove box, an NMR tube was charged with a solution of **241** (13.5 mg, 0.0540 mmol) in acetone-d_6 (~ 600 µl), and fitted with a rubber septum. The tube was removed from the drybox, and a solution of HBF_4 (54% in Et_2O, 7.8 µL, 0.057 mmol) was added via syringe. The sample was inverted several times, and the solution immediately turned brown. Complex **246** was characterized by NMR spectroscopy only, and was not isolated. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.62 (d, 1H, $J_{H1\text{-}OH} = 6.0$ Hz, -OH), 4.94 (dd, 1H, $J_{H1\text{-}OH} = 6.0$ Hz, $J_{H1\text{-}H2} = 9.3$ Hz, H_1), 4.31 (d, 1H, $J_{H2\text{-}H3syn} = 8.2$ Hz, H_{3syn}), 4.22 (ddd, 1H, $J_{H1\text{-}H2}$ = 9.3 Hz, $J_{H2\text{-}H3syn}$ = 8.2 Hz, $J_{H2\text{-}H3anti}$ = 11.7 Hz, H_2), 1.50 (s, 15H, $CpMe_5$), 1.43 (d, 1H, $J_{H2\text{-}H3anti}$ = 11.7 Hz, H_{3anti}).

As with complex **245**, the reactivity of **246** with acetylene was also investigated; acetylene gas was streamed through the acetone-d_6 solution of **246** at room temperature for several minutes, and the resulting solution was permitted to stand at room temperature for 30 minutes prior to NMR investigation which revealed a complicated mess and no evidence for seven-membered rings.

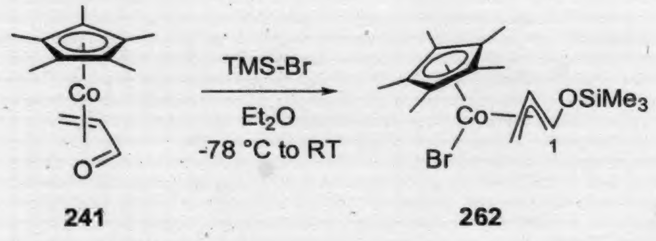

Co
O
241
1) $HBF_4 \cdot OEt_2$ / CH_2Cl_2 / -78 °C
2) C_2H_2 / CH_2Cl_2 / -78 °C to RT
3) KPF_6 / H_2O
Co^+ $^-PF_6$
7
1
Co^+ $^-PF_6$
247, <10 %

[Cp*Co(η^5-C_7H_8)]$_2$[PF$_6$]$_2$ (247): In the glove box, a Schlenk flask was charged with solid acrolein complex **241** (73.2 mg, 0.293 mmol), equipped with a stir-bar and septum, and removed to the Schlenk line. The complex was dissolved in degassed dichloromethane (10 mL) which was admitted via cannula. The green solution was cooled to -78 °C, and HBF_4 (54% in Et_2O, 40.0 µL, 0.290 mmol) was added via syringe. Acetylene was then streamed through the reaction for several minutes, and the reaction was then allowed to warm slowly to room temperature overnight (~ 19 h). The next morning, the solvent was removed *in vacuo*, and the brown residue was dissolved in distilled water (5 mL) and then filtered through Celite. The resulting orange filtrate was treated with saturated aqueous KPF_6 (2 mL), and the resulting orange precipitate was collected by vacuum filtration and air-dried. Only a very small amount of orange **247** was formed, and the complete sample was dissolved in CD_2Cl_2 for ^1H NMR interrogation. Upon standing overnight in the NMR tube, tiny crystals of **247** grew at room temperature which were suitable for X-ray crystallography. Unfortunately, no yield of **247** was recorded, although the yield is estimated at less than 10 mg. For full crystallographic data, request report #JMS0304 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3086 (m), 3049 (m), 3012 (m), 2972 (m), 2917 (s), 1569 (w), 1485 (s), 1430 (m), 1388 (s), 1358 (m), 1336 (m), 1312 (m), 1259 (m), 1233 (m), 1172 (w), 1159 (w), 1125 (w), 1075 (m), 1031 (m), 996 (w), 984 (m), 976 (m), 912 (w), 894 (w), 875 (s), 829 (s), 774 (m), 740 (m), 668 (w), 626 (w); ^1H NMR (400 MHz, CD_2Cl_2) δ 6.36 (ddd, 1H, $J_{H2-H3} = 7.0$ Hz, $J_{H3-H4} = 6.7$ Hz, $J_{H(1or5)-H3} = 1.4$ Hz, H_3), 5.10 (dd, 1H, $J_{H4-H5} = 8.3$ Hz, $J_{H3-H4} = 6.7$ Hz, H_4), 4.83 (dd, 1H, $J_{H2-H3} = 7.0$ Hz, $J_{H1-H2} = 9.3$ Hz, H_2), 4.14 (tdd, 1H, $J_{H4-H5} = J_{H5-H6eq} = 8.3$ Hz, $J_{H5-H6ax} = 4.4$ Hz, $J_{H5-H(3or7)} = 1.4$ Hz, H_5), 4.04 (ddd, 1H, $J_{H1-H2} = 9.3$ Hz, $J_{H1-H7} = 3.3$ Hz, $J_{H1-H(3or6eq)} = 1.3$ Hz, H_1), 2.91 (m, 1H, $J_{H1-H7} = 3.3$ Hz, $J_{H6ax-H7} = 9.9$ Hz, H_7), 1.89 (m, 1H, $J_{H6ax-H6eq} = 14.8$ Hz, $J_{H5-H6eq} = 8.3$ Hz, H_{6eq}), 1.83 (s, 15H, $CpMe_5$), -0.07 (ddd, $J_{H6ax-H6eq} = 14.8$ Hz, 1H, $J_{H6ax-H7} = 9.9$ Hz, $J_{H5-H6ax} = 4.4$ Hz, H_{6ax}); ^1H-^1H GCOSY (400 MHz, CD_2Cl_2) δ 6.36 $\leftrightarrow$ δ 5.10, δ 4.83; δ 5.10 $\leftrightarrow$ δ 4.14; δ 4.83 $\leftrightarrow$ δ 4.04; δ 4.14 $\leftrightarrow$ δ 1.89, δ -0.07; δ 2.91 $\leftrightarrow$ δ -0.07; δ 1.89 $\leftrightarrow$ δ -0.07.

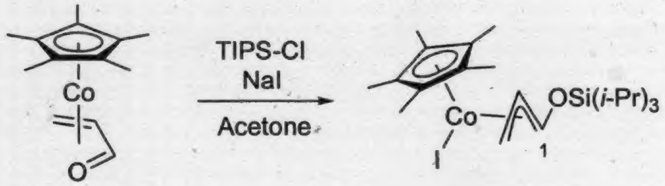


241 **261**

Cp*Co(III) 1-trimethylsiloxyallyl chloride (261): In the glove box, a Schlenk tube equipped with a stir-bar and rubber septum was charged with a solution of **241** (75.3 mg, 0.301 mmol) in diethyl ether (5 mL). The solution was removed to the Schlenk line and placed under an argon atmosphere, and cooled to -78 °C in a dry ice / acetone bath. Trimethylsilyl chloride (45 µL, 0.35 mmol) was added by syringe, and the reaction was allowed to warm to room temperature. No colour change was observed until the reaction neared room temperature, at which point the solution became purple. After stirring for an additional hour at room temperature, the solvent was removed *in vacuo*, and the residue was returned to the glove box. The residue was dissolved in a minimal amount of pentane/diethyl ether (~ 3:1, total volume ~ 0.5 mL), and filtered through a small amount of Celite. Cooling in the glove box overnight at -34 °C afforded purple microcrystalline **261** (87.4 mg, 0.244 mmol, 81%). IR (microscope, cm^{-1}) 3030 (w), 2957 (m), 2905 (w), 1510 (m), 1484 (w), 1442 (w), 1373 (m), 1264 (s), 1252 (s), 1239 (s), 1193 (s), 1152 (s), 1074 (m), 1025 (w), 964 (m), 947 (m), 900 (s), 872 (s), 850 (s), 828 (s), 783 (m), 759 (m), 699 (m); ^{1}H NMR (500 MHz, C_6D_6) δ 5.73 (d, 1H, $J_{H1\text{-}H2} = 9.1$ Hz, H_1), 3.74 (apparent dt, 1H, $J_{H1\text{-}H2} = 9.1$ Hz, $J_{H2\text{-}H3\mathit{anti}} = 12.4$ Hz, $J_{H2\text{-}H3\mathit{syn}} = 8.2$ Hz, H_2), 3.40 (d, 1H, $J_{H2\text{-}H3\mathit{syn}} = 8.2$ Hz, $H_{3\mathit{syn}}$), 2.57 (dd, 1H, $J_{H2\text{-}H3\mathit{anti}} = 12.4$ Hz, $J_{H3\mathit{syn}\text{-}H3\mathit{anti}} = 0.8$ Hz, $H_{3\mathit{anti}}$), 1.31 (s, 15H, $CpMe_5$), 0.23 (s, 9H, $SiMe_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 111.6 (C_1), 93.3 ($\underline{C_5}Me_5$), 83.1 (C_2), 47.5 (C_3), 9.3 ($C_5\underline{Me_5}$), -0.4 ($SiMe_3$). Analysis calculated for $C_{16}H_{28}ClCoSiO$: C, 53.55; H, 7.86; found: C, 53.98; H, 7.86.



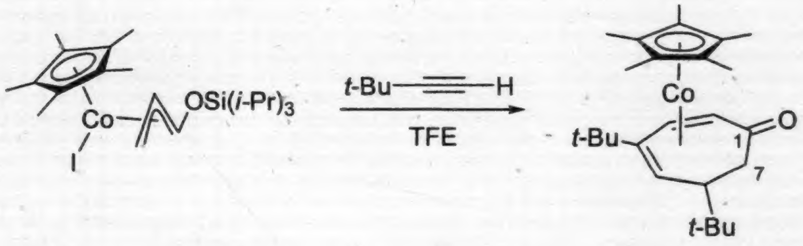
Cp*Co(III) 1-trimethylsiloxyallyl bromide (262): In the glove box, a Schlenk tube equipped with a stir-bar and rubber septum was charged with a solution of **241** (73.2 mg, 0.293 mmol) in diethyl ether (5 mL). The solution was removed to the Schlenk line, placed under an argon atmosphere, and cooled to -78 °C in a dry ice/acetone bath. Trimethylsilyl bromide (45 µL, 0.341 mmol) was added via syringe, and an immediate colour change from green to purple was observed. The reaction was allowed to warm to room temperature and, after stirring for an additional 15 minutes at room temperature, the solvent was removed *in vacuo.* The residue was returned to the glove box, dissolved in a minimal amount of pentane/diethyl ether (~ 3:1, total volume ~ 0.5mL), and filtered through a small amount of Celite. Cooling in the glove box overnight at -34 °C furnished purple microcrystalline **262** (98.3 mg, 0.244 mmol, 83%). For full crystallographic data, request report #JMS0327 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3031 (w), 2975 (w), 2955 (w), 2903 (w), 1510 (m), 1483 (w), 1443 (w), 1418 (w), 1379 (m), 1374 (w), 1355 (w), 1263 (s), 1253 (s), 1239 (m), 1193 (s), 1156 (s), 1074 (w), 1027 (w), 964 (m), 945 (m), 901 (s), 872 (s), 852 (s), 828 (m), 783 (m), 757 (w), 693 (w); ^{1}H NMR (500 MHz, C_6D_6) δ 6.06 (d, 1H, $J_{H1\text{-}H2}$ = 9.0 Hz, H_1), 3.60 (apparent dt, 1H, $J_{H1\text{-}H2}$ = 9.0 Hz, $J_{H2\text{-}H3\mathit{anti}}$ = 12.4 Hz, $J_{H2\text{-}H3\mathit{syn}}$ = 8.2 Hz, H_2), 3.28 (d, 1H, $J_{H2\text{-}H3\mathit{syn}}$ = 8.2 Hz, $H_{3\mathit{syn}}$), 2.80 (d, 1H, $J_{H2\text{-}H3\mathit{anti}}$ = 12.4 Hz, $H_{3\mathit{anti}}$), 1.37 (s, 15H, CpMe$_5$), 0.23 (s, 9H, SiMe$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 109.2 (C_1), 93.2 ($\underline{C_5}Me_5$), 82.5 (C_2), 45.1 (C_3), 9.6 ($C_5\underline{Me_5}$), -0.4 (SiMe$_3$). Analysis calculated for $C_{16}H_{28}BrCoSiO$: C, 47.65; H, 7.00; found: C, 48.01; H, 6.89.



241 **263**

Cp*Co(III) 1-tri(*iso*-propyl)siloxyallyl iodide (263): In the glove box, a Schlenk flask equipped with a stir-bar and rubber septum was charged with a solution of **241** (155.5 mg, 0.6214 mmol) and sodium iodide (175.1 mg, 1.168 mmol) in acetone (10 mL). The solution was removed to the Schlenk line and placed under an argon atmosphere. Triisopropylsilyl chloride (150 µL, 0.701 mmol) was added via syringe, and an immediate colour change from green to purple was observed. The reaction was allowed to stir at room temperature for 15 minutes and the solvent was then removed *in vacuo*. The residue was returned to the glove box, dissolved in a minimal amount of pentane, and filtered through a small amount of Celite. Purple solid **263** was obtained upon crystallization overnight at -80 °C, and **263** (269.4 mg, 0.5040 mmol, 81%) was isolated upon cannula-removal of the supernatant and subsequent vacuum-drying. IR

(microscope, cm^{-1}) 3068 (w), 2941 (s), 2866 (s), 1811 (w), 1511 (m), 1461 (s), 1379 (m), 1241 (m), 1173 (m), 1072 (w), 1026 (w), 996 (w), 949 (m), 920 (m), 884 (m), 833 (m), 794 (m), 680 (m), 657 (m); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.09 (apparent dt, 1H, $J_{H1\text{-}H2}$ = 9.1 Hz, $J_{H1\text{-}H3\mathit{anti}}$ = 1.0 Hz, $J_{H1\text{-}H3\mathit{syn}}$ = 0.7 Hz, H_1), 3.60 (ddd, 1H, $J_{H1\text{-}H2}$ = 9.1 Hz, $J_{H2\text{-}H3\mathit{anti}}$ = 12.3 Hz, $J_{H2\text{-}H3\mathit{syn}}$ = 8.3 Hz, H_2), 3.28 (ddd, 1H, $J_{H2\text{-}H3\mathit{syn}}$ = 8.3 Hz, $J_{H1\text{-}H3\mathit{syn}}$ = 0.7 Hz, $J_{H3\mathit{syn}\text{-}H3\mathit{anti}}$ = 1.4 Hz, $H_{3\mathit{syn},}$), 2.69 (ddd, 1H, $J_{H2\text{-}H3\mathit{anti}}$ = 12.3 Hz, $J_{H1\text{-}H3\mathit{anti}}$ = 1.0 Hz, $J_{H3\mathit{syn}\text{-}H3\mathit{anti}}$ = 1.4 Hz, $H_{3\mathit{anti}}$), 1.74 (s, 15H, $CpMe_5$), 1.27 (m, 3H, -$SiC\underline{H}(CH_3)$), 1.18 (d, 9H, J = 7.3 Hz, -$SiCH(C\underline{H}_3)$), 1.16 (d, 9H, J = 7.3 Hz, -$SiCH(C\underline{H}_3)$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 105.8 (C_1), 93.4 ($\underline{C}_5Me_5$), 82.0 (C_2), 41.4 (C_3), 18.2 (-$SiCH(\underline{C}H_3)$), 18.1 (-$SiCH(\underline{C}H_3)$), 12.4 (-$Si\underline{C}H(CH_3)$), 10.7 ($C_5\underline{Me}_5$); HMQC (500 MHz, CD_2Cl_2) δ 105.8 ↔ δ 6.09; δ 82.0 ↔ δ 3.60; δ 41.4 ↔ δ 3.28, δ 2.69; δ 18.2, 18.1 (unresolved) ↔ δ 1.18, 1.16 (unresolved); δ 12.4 ↔ δ 1.27; δ 10.7 ↔ δ 1.74. Analysis calculated for $C_{22}H_{40}CoIOSi$: C, 49.44; H, 7.54; found: C, 49.48; H, 7.52.

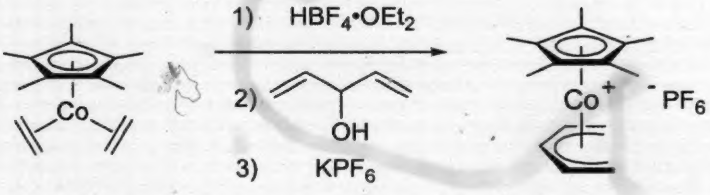


263 **267**

Cp*Co(I) 4,6-di-*t*-butylcyclohepta-2,4-dienone (267): In the glove box, a Schlenk tube was charged with **263** (68.2 mg, 0.128 mmol), and equipped with a stir-bar and rubber septum. The tube was removed to the Schlenk line, and placed under an argon atmosphere. Dry, degassed 2,2,2-trifluoroethanol (5 mL) was added via cannula, resulting in a brick red-brown solution. To this solution, *t*-butylacetylene (100 µL, 0.812 mmol) was added via syringe, and the reaction immediately became greenish-brown. The reaction was stirred at room temperature for 1 hour, and the solvent was then removed by rotary evaporation. The residue was applied to a silica gel column with dichloromethane, and then chromatographed with methanol (3%) in dichloromethane. As the eluent passed through the column, the product band became deep purple. The product was collected, and concentrated by rotary evaporation, and then redissolved in a minimal amount of pentane. The purple pentane solution was filtered through Celite, and cooled to -80 °C to induce crystallization. **267** (35.1 mg, 0.0845 mmol, 66%) was obtained as a purple crystalline solid. For full crystallographic data, request report #JMS0337 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3201 (w), 3017 (s), 2972 (s), 2948 (s), 2907 (s), 2866 (m), 2834 (m), 1688 (w), 1612 (s), 1494 (s), 1454 (m), 1430 (m), 1384 (m), 1360 (m), 1319 (m), 1291 (m), 1265 (m), 1245 (w), 1215 (m), 1156 (m), 1351 (m), 1114 (w), 1072 (w), 1029 (s), 975 (s), 955 (m), 937 (m), 901 (m), 873 (m), 846 (w), 809 (w), 701 (w), 666 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (dd, 1H, $J_{H2\text{-}H3}$ = 6.3 Hz, $J_{H3\text{-}H5}$ = 1.0 Hz, H_3), 2.99 (m, 1H, H_5), 2.40 (dd, 1H, $J_{H2\text{-}H3}$ = 6.3 Hz, $J_{H2\text{-}H7\mathit{endo}}$ = 2.1 Hz, H_2,), 2.09 (ddd, 1H, $J_{H6\text{-}H3\mathit{exo}}$ = 12.8 Hz, $J_{H6\text{-}H7\mathit{endo}}$ = 3.4 Hz, $J_{H5\text{-}H6}$ = 1.6 Hz, H_6), 1.67 (s, 15H, $CpMe_5$), 1.64 (ddt, 1H, $J_{H7\mathit{endo}\text{-}H7\mathit{exo}}$ = 10.7 Hz, $J_{H6\text{-}H7\mathit{endo}}$ = 3.4 Hz, $J_{H2\text{-}H7\mathit{endo}}$ = 2.1 Hz, $J_{H5\text{-}H7\mathit{endo}}$ = 2.1 Hz, $H_{7\mathit{endo}}$), 1.28 (s, 9H, $C(C\underline{H}_3)_3$), 0.93 (dd, 1H, $J_{H6\text{-}H3\mathit{exo}}$ = 12.8 Hz, $J_{H7\mathit{endo}\text{-}H7\mathit{exo}}$ = 10.7 Hz, $H_{7\mathit{exo}}$), 0.87 (s, 9H, $C(C\underline{H}_3)_3$); ^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) δ 5.22 ↔ δ 2.99, δ 2.40; δ 2.99 ↔ δ 2.09, δ 1.64; δ 2.40 ↔ δ 1.64; δ 2.09 ↔ δ 1.64, δ 0.93; δ 1.64 ↔ δ 0.93; ^{13}C NMR

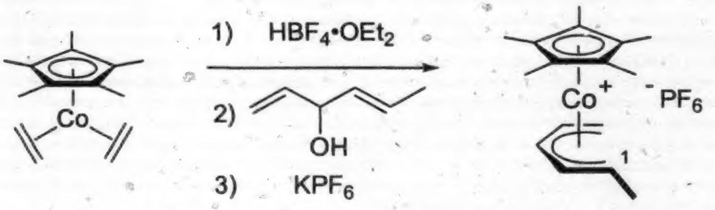
(100 MHz, $CDCl_3$) δ 206.2 (C_1), 110.1 (C_4), 90.3 ($\underline{C}_5Me_5$), 81.1 (C_3), 62.3 (C_6), 52.8 (C_2), 51.0 (C_5), 38.2 (C_7), 35.3 ($\underline{C}(CH_3)_3$), 35.2 ($\underline{C}(CH_3)_3$), 31.1 ($C(\underline{C}H_3)_3$), 27.9 ($C(\underline{C}H_3)_3$), 9.6 ($C_5\underline{Me}_5$); HMQC (400 MHz, $CDCl_3$) δ 81.1 ↔ δ 5.22; δ 62.3 ↔ δ 2.09; δ 52.8 ↔ δ 2.40; δ 51.0 ↔ δ 2.99; δ 38.2 ↔ δ 1.64, 0.93; δ 31.1 ↔ δ 1.28; δ 27.9 ↔ δ 0.87; δ 9.6 ↔ δ 1.67. Analysis calculated for $C_{25}H_{39}CoO$: C, 72.44; H, 9.48; found: C, 72.25; H, 7.69. Additionally, electrospray mass spectrometry (methanol solvent) was performed, and $[M+H]^+$ was detected: calculated mass for $C_{25}H_{40}CoO$ = 415.24057 amu; observed = 415.24032 amu.

Part D: Chapter 4 Experimental Section



43 **451**

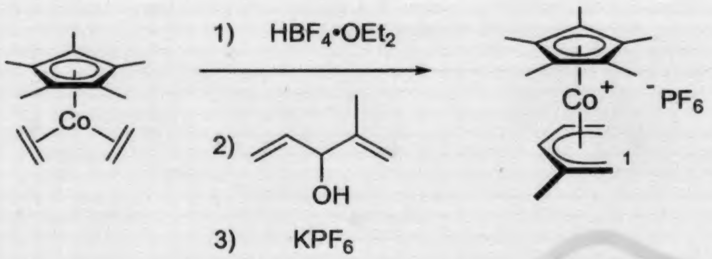
Cp*Co(III) pentadienyl hexafluorophosphate (451): A Schlenk tube was charged with a solution of **43** (26.1 mg, 0.104 mmol) in acetone (~ 1 mL) in the glove box, and equipped with a stir-bar and septum. The solution was removed to the Schlenk line, placed under an argon atmosphere, and cooled to -78 °C. Tetrafluoroboric acid (54 % in diethyl ether, 15.1 μL, 0.110 mmol) was added by syringe, and the reaction was stirred at -78 °C for 30 min. 1,4-Pentadien-3-ol (11.2 μL, 0.115 mmol) was then added, and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed *in vacuo*, and the residue was taken up in several milliliters of distilled water, and filtered through Celite. Several milliliters of a saturated aqueous KPF_6 solution was added to the orange-red solution, causing immediate precipitation of **451**, which was recovered by vacuum filtration. The crude **451** was purified by silica gel chromatography, eluting with a 3% methanol-dichloromethane mixture. Removal of solvent *in vacuo* afforded **451** as an orange solid (28.2 mg, 0.0694 mmol, 67%) which was of suitable purity for use in subsequent reactions. Analytically pure material (25.4 mg, 0.0625 mmol, 60%) was obtained by pinhole diffusion crystallization (ether into dichloromethane), although repeated efforts to grow crystals suitable for X-Ray analysis proved fruitless. IR (microscope, cm^{-1}) 3072 (w), 2989 (w), 2919 (w), 1559 (w), 1540 (w), 1516 (m), 1473 (m), 1455 (m), 1430 (m), 1390 (s), 1078 (w), 1031 (m), 937 (w), 918 (m), 877 (m), 856 (m); ^1H NMR (400 MHz, Acetone-d_6) δ 6.52 (tp, 1H, $J_{H2\text{-}H3}$ = 6.9 Hz, $J_{H1\text{-}H3}$ = 1.0 Hz, H_3), 5.35 (ddd, 2H, $J_{H1\mathit{anti}\text{-}H2}$ = 12.4 Hz , $J_{H1\mathit{syn}\text{-}H2}$ = 9.7 Hz, $J_{H2\text{-}H3}$ = 6.9 Hz, H_2), 3.50 (ddd, 2H, $J_{H1\mathit{syn}\text{-}H2}$ = 9.7 Hz, $J_{H1\mathit{syn}\text{-}H1\mathit{anti}}$ = 2.8 Hz, $J_{H1\mathit{syn}\text{-}H3}$ = 1.0 Hz, $H_{1\mathit{syn}}$), 2.01 (s, 15H, $CpMe_5$), 1.98 (ddd, 2H, $J_{H1\mathit{anti}\text{-}H2}$ = 12.4 Hz, $J_{H1\mathit{syn}\text{-}H1\mathit{anti}}$ = 2.8 Hz, $J_{H1\mathit{anti}\text{-}H3}$ = 1.0 Hz, $H_{1\mathit{anti}}$); ^{13}C NMR (100 MHz, Acetone-d_6) δ 100.6 ($\underline{C}_5Me_5$ or C_2), 100.4 ($\underline{C}_5Me_5$ or C_2), 100.0 (C_3), 65.5 (C_1), 9.9 ($C_5\underline{Me}_5$); HMQC (500 MHz, Acetone-d_6) δ 100.6 or 100.4 ↔ δ 5.35; δ 100.0 ↔ δ 6.52; δ 65.5 ↔ δ 3.50, δ 1.98; δ 9.9 ↔ δ 2.01. Analysis calculated for $C_{15}H_{22}CoPF_6$: C, 44.35; H, 5.46; found: C, 44.72; H, 5.71. Electrospray high-resolution mass spectrometry; mass calculated for $C_{15}H_{22}Co$: 261.10480; found: 261.10493.



43 **430**

Cp*Co(III) 1-methylpentadienyl hexafluorophosphate (430): A Schlenk tube was charged with a solution of **43** (229.9 mg, 0.9186 mmol) in acetone (10 mL) in the glove box, and equipped with a stir-bar and septum. The solution was removed to the Schlenk line, placed under an Argon atmosphere, and cooled to - 78 °C. Tetrafluoroboric acid (54 % in diethyl ether) was added by syringe, and the reaction was stirred at -78 °C for 30min. 1,4-Hexadien-3-ol **443** (110 μL, mmol) was then added, and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed *in vacuo*, and the residue was taken up in several milliliters of distilled water, and filtered through Celite. Saturated aqueous KPF$_6$ (10 mL) was added to the orange-red solution inducing an immediate precipitation of **430**, which was recovered by vacuum filtration. The crude **430** was purified by silica gel chromatography, eluting with a 3% methanol-dichloromethane mixture. Removal of solvent *in vacuo* afforded **430** as an orange solid (291.2 mg, 0.6929 mmol, 75%) which was of suitable purity for use in subsequent reactions. Analytically pure material (197.6 mg, 0.4702 mmol, 51%) suitable for X-Ray diffraction study was further obtained by pinhole diffusion crystallization (ether into dichloromethane). For full crystallographic data, request report #JMS0423 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3133 (w), 2996 (w), 2969 (w), 2919 (w), 1579 (w), 1526 (w), 1491 (m), 1478 (m), 1455 (m), 1434 (m), 1382 (m), 1077 (w), 1020 (m), 958 (w), 935 (w), 877 (m), 842 (s), 747 (w); ^{1}H NMR (600 MHz, Acetone-d_6) δ 6.46 (t, 1H, $J_{\text{H2-H3}}$, $J_{\text{H3-H4}}$ = 6.9 Hz, H$_3$), 5.32 (dd, 1H, $J_{\text{H1-H2}}$ = 12.1 Hz , $J_{\text{H2-H3}}$ = 6.9 Hz, H$_2$), 5.18 (dddd, 1H, $J_{\text{H4-H5}\textit{anti}}$ = 11.9 Hz , $J_{\text{H4-H5}\textit{syn}}$ = 9.5 Hz, $J_{\text{H3-H4}}$ = 6.9 Hz, $J_{\text{H2-H4}}$ = 0.7, H$_4$), 3.39 (dd, 1H, $J_{\text{H4-H5}\textit{syn}}$ = 9.5 Hz, $J_{\text{H5}\textit{syn}\text{-H5}\textit{anti}}$ = 3.4 Hz, H$_{5\textit{syn}}$), 2.37 (dq, 1H, $J_{\text{H1-H2}}$ = 12.1 Hz, $J_{\text{H1-CH3}}$ = 6.3 Hz, H$_1$), 1.97 (ddd, 1H, $J_{\text{H4-H5}\textit{anti}}$ = 11.9 Hz, $J_{\text{H5}\textit{syn}\text{-H5}\textit{anti}}$ = 3.4 Hz, $J_{\text{H3-H5}\textit{anti}}$ = 0.7 Hz, H$_{5\textit{anti}}$), 1.95 (s, 15H, CpMe$_5$), 1.56 (dd, 3H, $J_{\text{H1-CH3}}$ = 6.3 Hz, $J_{\text{H2-CH3}}$ = 0.7 Hz, CH$_3$); ^{13}C NMR (125 MHz, Acetone-d_6) δ 100.4 (C$_2$ and C$_4$, two resonances observed), 99.2 ($\underline{\text{C}_5}\text{Me}_5$), 95.5 (C$_3$), 84.9 (C$_1$), 64.5 (C$_5$), 18.6 (CH$_3$), 9.9 ($\text{C}_5\underline{\text{Me}_5}$); HMQC (600 MHz, Acetone-d_6) δ 100.4 ↔ δ 5.18, δ 5.32; δ 95.5 ↔ δ 6.46; δ 84.9 ↔ δ 2.37; δ 64.5 ↔ δ

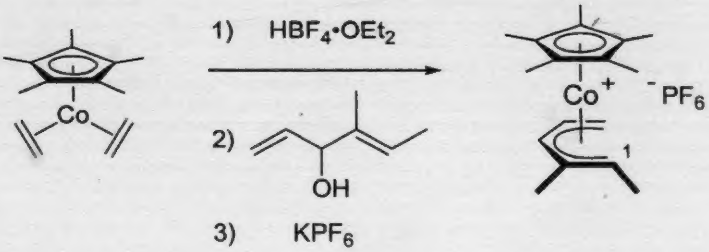
3.39, δ 1.97; δ 18.6 ↔ δ 1.56; δ 9.7 ↔ δ 1.95. HMBC (600 MHz, Acetone-d_6) δ 100.4 ↔ δ 6.46, δ 5.32, δ 5.18, δ 3.39, δ 1.56; δ 99.2 ↔ δ 1.95; δ 95.5 ↔ δ 3.39, δ 2.37; δ 84.9 ↔ δ 6.46, δ 1.56; δ 64.5 ↔ δ 6.46, δ 1.97; δ 18.6 ↔ δ 5.32, δ 2.37. Analysis calculated for $C_{16}H_{24}CoPF_6$: C, 45.73; H, 5.76; found: C, 45.55; H, 5.87. Electrospray high-resolution mass spectrometry; mass calculated for $C_{16}H_{24}Co$: 275.12045; found: 275.12042.



43 **452**

Cp*Co(III) 2-methylpentadienyl hexafluorophosphate (452): A Schlenk tube was charged with a solution of **43** (25.5 mg, 0.102 mmol) in acetone (~ 1 mL) in the glove box, and equipped with a stir-bar and septum. The solution was removed to the Schlenk line, placed under an argon atmosphere, and cooled to -78 °C. Tetrafluoroboric acid (54 % in diethyl ether, 14.7 μL, 0.107 mmol) was added by syringe, and the reaction was stirred at -78 °C for 30min. 2-Methyl-1,4-pentadien-3-ol **444** (12.5 μL, 0.111 mmol) was then added, and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed *in vacuo*, and the residue was taken up in several milliliters of distilled water and filtered through Celite. Several milliliters of a saturated aqueous KPF_6 solution was added to the orange-red solution. Orange-red **452**

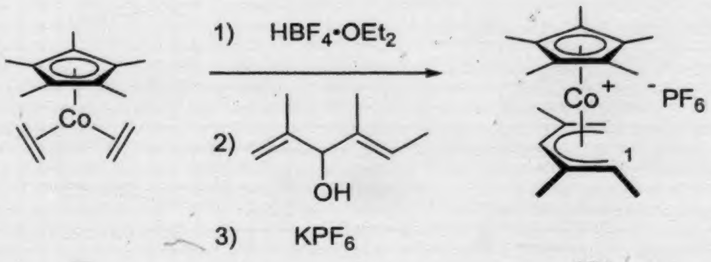
precipitated immediately, and was collected by vacuum filtration. The crude **452** was purified by silica gel chromatography, eluting with a 3% methanol-dichloromethane mixture. Removal of solvent *in vacuo* afforded **452** as an orange solid (23.1 mg, 0.0550 mmol, 54%) which was of suitable purity for use in subsequent reactions. Analytically pure material suitable for X-Ray diffraction study was obtained by pinhole diffusion crystallization of a small amount of the crude product (ether into dichloromethane). For full crystallographic data, request report #JMS0452 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 2993 (w), 2918 (w), 1580 (w), 1510 (w), 1454 (m), 1430 (m), 1385 (m), 1252 (w), 1229 (w), 1160 (w), 1078 (w), 1028 (m), 981 (w), 932 (w), 910 (w), 877 (m), 849 (s), 673 (w); ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.40 (d, 1H, $J_{H3\text{-}H4}$ = 7.0 Hz, H_3), 5.31 (ddd, 1H, $J_{H4\text{-}H5\mathit{anti}}$ = 12.0 Hz, $J_{H4\text{-}H5\mathit{syn}}$ = 9.6 Hz, $J_{H3\text{-}H4}$ = 7.0 Hz, H_4), 3.57 (dd, 1H, $J_{H4\text{-}H5\mathit{syn}}$ = 9.6 Hz, $J_{H5\mathit{syn}\text{-}H5\mathit{anti}}$ = 3.0 Hz, $H_{5\mathit{syn}}$), 3.22 (dd, 1H, $J_{H1\mathit{syn}\text{-}H1\mathit{anti}}$ = 3.4 Hz, $J_{H1\mathit{syn}\text{-}H3}$ = 0.8 Hz, $H_{1\mathit{syn}}$), 2.21 (s, 3H, CH_3), 2.09 (ddd, 1H, $J_{H4\text{-}H5\mathit{anti}}$ = 12.0 Hz, $J_{H5\mathit{syn}\text{-}H5\mathit{anti}}$ = 3.0 Hz, $J_{H3\text{-}H5\mathit{anti}}$ = 0.8 Hz, $H_{5\mathit{anti}}$), 1.97 (s, 15H, $CpMe_5$), 1.68 (dd, 1H, $J_{H1\mathit{syn}\text{-}H1\mathit{anti}}$ = 3.4 Hz, $J_{H1\mathit{syn}\text{-}H3}$ = 0.6 Hz, $H_{1\mathit{anti}}$); ^{13}C NMR (125 MHz, Acetone-d_6) δ 114.0 (C_2), 99.9 ($\underline{C}_5Me_5$), 98.3 (C_3), 86.9 (C_4), 67.5 (C_5), 61.1 (C_1), 23.0 (CH_3), 9.8 ($C_5\underline{Me}_5$); HMQC (500 MHz, Acetone-d_6) δ 98.3 ↔ δ 6.40; δ 67.5 ↔ δ 3.57, δ 2.09; δ 61.1 ↔ δ 3.22, δ 1.68; δ 23.0 ↔ δ 2.21; δ 9.8 ↔ δ 1.97. HMBC (500 MHz, Acetone-d_6) δ 114.0 ↔ δ 5.31, δ 2.21; δ 99.9 ↔ δ 1.97; δ 98.3 ↔ δ 3.57, δ 3.22, δ 2.21, δ 2.09; δ 67.5 ↔ δ 6.40; δ 61.1 ↔ δ 6.40, δ 2.21; δ 23.0 ↔ δ 6.40, δ 3.22, δ 1.68. Analysis calculated for $C_{16}H_{24}CoPF_6$: C, 45.73; H, 5.76; found: C, 45.43; H, 5.74. Electrospray high-resolution mass spectrometry; mass calculated for $C_{16}H_{24}Co$: 275.12045; found: 275.12050.



43 **453**

Cp*Co(III) 1,2-dimethylpentadienyl hexafluorophosphate (453): A Schlenk tube was charged with a solution of **43** (22.0 mg, 0.0879 mmol) in acetone (~ 1 mL) in the glove box, and equipped with a stir-bar and septum. The solution was removed to the Schlenk line, placed under an argon atmosphere, and cooled to - 78 °C. Tetrafluoroboric acid (54 % in diethyl ether, 12.7 μL, 0.092 mmol) was added by syringe, and the reaction was stirred at -78 °C for 30min. 4-Methyl-1,4-hexadien-3-ol **445** (12.2 μL, 0.0934 mmol) was then added, and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed *in vacuo*, and the residue was taken up in several milliliters of distilled water, and filtered through Celite. Aqueous KPF_6 was added to the orange-red solution, causing immediate precipitation of **453**, which was recovered by vacuum filtration. The crude **453** was purified by silica gel chromatography, eluting with a 3% methanol-dichloromethane mixture. Removal of solvent *in vacuo* afforded **453** as an orange solid (22.5 mg, 0.0518 mmol, 59%) which was of suitable purity for use in subsequent reactions. Analytically pure material suitable for X-Ray diffraction study was obtained by pinhole diffusion (ether into dichloromethane) crystallization of a small portion of the chromatographic product. For full crystallographic data, request report #JMS0520 from the X-Ray Crystallography Laboratory at the University of Alberta

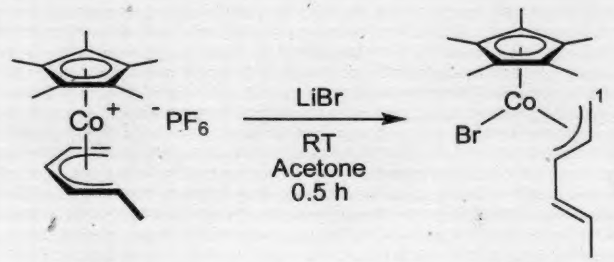
Department of Chemistry. IR (microscope, cm^{-1}) 3073(w), 3005 (w), 2974 (w), 2925 (w), 1990 (w), 1940 (w), 1858 (w), 1614 (w), 1575 (w), 1465 (m), 1433 (m), 1392 (s), 1365 (w), 1297 (w), 1262 (w), 1225 (w), 1159 (w), 1130 (w), 1087 (w), 1074 (w), 1029 (m), 994 (w), 973 (w), 948 (w), 913 (m), 853 (s), 785 (w), 740 (w); ^1H NMR (600 MHz, Acetone-d_6) δ 6.39 (d, 1H, $J_{H3\text{-}H4}$ = 7.3 Hz, H_3), 5.07 (ddd, 1H, $J_{H4\text{-}H5anti}$ = 12.2 Hz, $J_{H4\text{-}H5syn}$ = 10.0 Hz, $J_{H3\text{-}H4}$ = 7.3 Hz, H_4), 3.45 (ddd, 1H, $J_{H4\text{-}H5syn}$ = 10.0 Hz, $J_{H5syn\text{-}H5anti}$ = 3.5 Hz, $J_{H3\text{-}H5syn}$ = 0.6 Hz, H_{5syn}), 2.35 (ddd, 1H, $J_{H4\text{-}H5anti}$ = 12.2 Hz, $J_{H5syn\text{-}H5anti}$ = 3.5 Hz, $J_{H3\text{-}H5anti}$ = 1.0 Hz, H_{5anti}), 2.19 (s, 3H, C_2-CH_3), 1.90 (s, 15H, $CpMe_5$), 1.71 (q, 1H, $J_{H1\text{-}C1CH3}$ = 6.6 Hz, H_1), 1.46 (d, 3H, $J_{H1\text{-}C1CH3}$ = 6.6 Hz, C_1-CH_3); ^{13}C NMR (100 MHz, Acetone-d_6) δ 111.9 (C_2), 99.4 (C_4), 98.8 ($\underline{C_5}Me_5$), 96.6 (C_3), 76.4 (C_1), 66.7 (C_5), 17.5 (C_2-CH_3), 14.9 (C_1-CH_3), 9.5 ($C_5\underline{Me_5}$); HMQC (600 MHz, Acetone-d_6) δ 99.4 ↔ δ 5.07; δ 96.6 ↔ δ 6.39; δ 76.4 ↔ δ 1.71; δ 66.7 ↔ δ 3.45, δ 2.35; δ 17.5 ↔ δ 2.19; δ 14.9 ↔ δ 1.46; δ 9.5 ↔ δ 1.90. HMBC (600 MHz, Acetone-d_6) δ 111.9 ↔ δ 5.07, δ 2.19, δ 1.71, δ 1.46; δ 99.4 ↔ δ 3.45; δ 98.8 ↔ δ 1.90; δ 96.6 ↔ δ 3.45, δ 2.19, δ 1.71; δ 76.4 ↔ δ 6.39, δ 2.19, δ 1.46; δ 66.7 ↔ δ 6.39; δ 17.5 ↔ δ 6.39, δ 1.71; δ 14.9 ↔ δ 1.71. Analysis calculated for $C_{17}H_{26}CoPF_6$: C, 47.02; H, 6.03; found: C, 46.93; H, 6.13. Electrospray high-resolution mass spectrometry; mass calculated for $C_{17}H_{26}Co$: 289.13610; found: 289.13615.



43 **454**

Cp*Co(III) 1,2,4-trimethylpentadienyl hexafluorophosphate (454): A Schlenk tube was charged with a solution of **43** (21.7 mg, 0.0867 mmol) in acetone (~ 1 mL) in the glove box, and equipped with a stir-bar and septum. The solution was removed to the Schlenk line, placed under an argon atmosphere, and cooled to - 78 °C. Tetrafluoroboric acid (54 % in diethyl ether, 12.5 µL, 0.0907 mmol) was added by syringe, and the reaction was stirred at -78 °C for 30min. 2,4-Dimethyl-1,4-hexadien-3-ol **446** (13.6 µL, 0.0927 mmol) was then added, and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed *in vacuo*, and the residue was taken up in several milliliters of distilled water, and filtered through Celite. Several milliliters of a saturated aqueous KPF_6 solution was added to the orange-red solution, causing immediate precipitation of **454**, which was recovered by vacuum filtration. The crude **454** was purified by silica gel chromatography, eluting with a 3% methanol-dichloromethane mixture. Removal of solvent *in vacuo* afforded **454** as an orange solid (11.5 mg, 0.0257 mmol, 30%) which was of suitable purity for use in subsequent reactions. Analytically pure material suitable for X-Ray diffraction study was obtained by pinhole diffusion crystallization (ether into dichloromethane). For full crystallographic data, request report #JMS0570 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1})

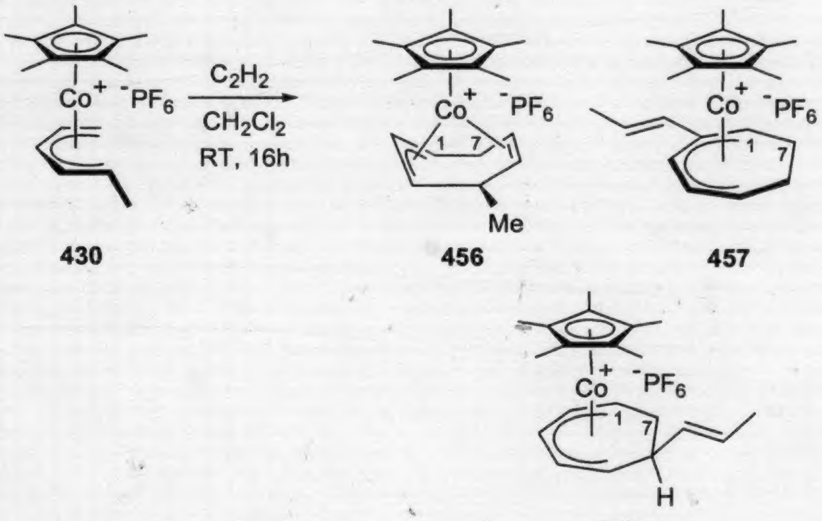
3137 (w), 3058 (w), 2994 (m), 2973 (m), 2916 (m), 1868 (w), 1576 (w), 1479 (s), 1452 (s), 1434 (s), 1409 (m), 1383 (s), 1314 (w), 1266 (w), 1209 (w), 1161 (w), 1118 (w), 1075 (m), 1028 (s), 976 (w), 959 (w), 937 (m), 851 (s), 795 (m), 777 (w), 733 (w); ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.34 (s, 1H, H_3), 3.16 (d, 1H, $J_{H5syn\text{-}H5anti}$ = 4.2 Hz, H_{5syn}), 2.19 (s, 3H, C_2-CH_3), 2.16 (s, 3H, C_4-CH_3), 2.07 (d, 1H, $J_{H5syn\text{-}H5anti}$ = 4.2 Hz, H_{5anti}), 1.86 (s, 15H, $CpMe_5$), 1.77 (q, 1H, $J_{H1\text{-}C1CH3}$ = 6.6 Hz, H_1), 1.45 (d, 3H, $J_{H1\text{-}C1CH3}$ = 6.6 Hz, C_1-CH_3); ^{13}C NMR (125 MHz, Acetone-d_6) δ 112.1 (C_4), 111.0 (C_2), 98.4 ($\underline{C_5}Me_5$), 95.1 (C_3), 79.1 (C_1), 61.8 (C_5), 23.8 (C_4-CH_3),17.8 (C_2-CH_3), 15.1 (C_1-CH_3), 9.5 ($C_5\underline{Me_5}$); HMQC (500 MHz, Acetone-d_6) δ 95.1 ↔ δ 6.34; δ 79.1 ↔ δ 1.77; δ 61.8 ↔ δ 3.16, δ 2.07; δ 23.8 ↔ δ 2.16; δ 17.8 ↔ δ 2.19; δ 15.1 ↔ δ 1.45; δ 9.5 ↔ δ 1.86. HMBC (500 MHz, Acetone-d_6) δ 112.1 ↔ δ 2.16; δ 111.0 ↔ δ 2.19, δ 1.77, δ 1.45; δ 98.4 ↔ δ 1.86; δ 95.1 ↔ δ 3.16, δ 21.9, δ 2.16, δ 1.77; δ 79.1 ↔ δ 6.34, δ 2.19, δ 1.45; δ 61.8 ↔ δ 6.34, δ 2.16; δ 23.8 ↔ δ 6.34, δ 3.16, δ2.07; δ 17.8 ↔ δ 6.34, δ 1.77. Analysis calculated for $C_{18}H_{28}CoPF_6$: C, 48.22; H, 6.29; found: C, 48.38; H, 6.39. Electrospray high-resolution mass spectrometry; mass calculated for $C_{18}H_{28}Co$: 303.15175; found: 303.15162.



430 **190b**

Cp*Co η^3-*trans*-hexa-2,4-dien-1-yl bromide (190b): In the glove box, lithium bromide (73.2 mg, 0.842 mmol) was added at room temperature to a stirring solution of pentadienyl complex **430** (81.6 mg, 0.194 mmol) in acetone. The solution changed in colour from red to purple over several minutes. The reaction mixture was maintained at room temperature for 30 minutes, at which point the solvent was removed *in vacuo*. The purple residue was dissolved in a minimal amount of benzene (2 mL) and filtered through a plug of Celite. Removal of solvent and drying under vacuum afforded complex **190b** (68.9 mg, 0.194 mmol) as a purple solid. A small amount of **190b** was crystallized at -34 °C from a mixture of diethyl ether and pentane to afford crystals suitable for X-ray crystallography. For full crystallographic data, request report #JMS0509 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. ^{1}H NMR (300 MHz, C_6D_6) δ 6.10 (dqd, 1H, $J_{H4\text{-}H5}$ = 15.2 Hz, $J_{H5\text{-}H6}$ = 6.9 Hz, $J_{H3\text{-}H5}$ = 0.8 Hz, H_5), 5.52 (ddq, 1H, $J_{H4\text{-}H5}$ = 15.2 Hz, $J_{H3\text{-}H4}$ = 10.8 Hz, $J_{H4\text{-}H6}$ = 1.6 Hz, H_4), 4.47 (t, 1H, $J_{H2\text{-}H3}$ = $J_{H3\text{-}H4}$ = 10.9 Hz, H_3), 3.71 (d, 1H, $J_{H1syn\text{-}H2}$ = 7.3 Hz, H_{1syn}), 3.62 (app. t of d, 1H, $J_{H1syn\text{-}H2}$ = 7.3 Hz, $J_{H1anti\text{-}H2}$ = 12.2 Hz, $J_{H2\text{-}H3}$ = 10.9 Hz, H_2), 3.38 (d, 1H, $J_{H1anti\text{-}H2}$ = 12.2 Hz, H_{1anti}), 1.36 (dd, 3H, $J_{H4\text{-}H6}$ = 1.6 Hz, $J_{H5\text{-}H6}$ = 6.9 Hz, H_6), 1.26 (s, 15H, $CpMe_5$); ^{1}H-^{1}H GCOSY (500 MHz, C_6D_6) δ 6.10 ↔ δ 5.52, δ 1.36; δ 5.52 ↔ δ 4.47, δ

1.36; δ 4.47 ↔ δ 3.62, δ 3.38, δ 1.36; δ 3.71 ↔ δ 3.62; δ 3.62 ↔ δ 3.38; ^{13}C NMR (125 MHz, C_6D_6) δ 135.0 (C_4), 128.1 (C_5), 94.4 ($\underline{C_5}Me_5$), 92.8 (C_2), 78.0 (C_3), 54.1 (C_1), 19.4 (C_6), 9.9 ($C_5\underline{Me_5}$).



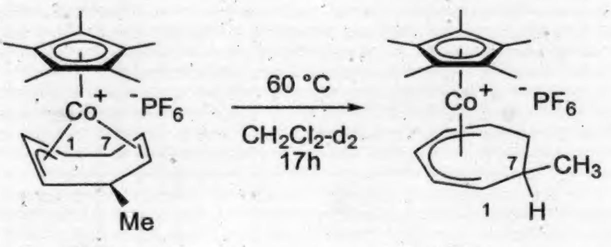
430

456

457

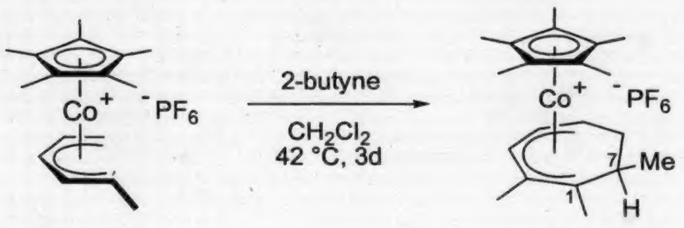
458

Cp*Co(III) η^3,η^2-4-methylcycloheptadienyl hexafluorophosphate (456): A test tube was charged with a solution of **430** (39.5 mg, 0.0940 mmol) in freshly distilled dichloromethane (10 mL). The tube was fitted with a septum, and acetylene was streamed through the solution for ~15 minutes, to ensure saturation. The solution was maintained at room temperature for 19 h, before the removal of solvent by rotary evaporation. The orange-red residue was chromatographed on silica gel with a 4% methanol in dichloromethane mixture, affording a red solid (41.3 mg, 0.0925 mmol, 98%) which was comprised primarily of **456**, but contained traces (less than 5% each by ^{1}H NMR integration) of **457** and **458**. A small amount of **456** suitable for X-ray diffraction analysis was obtained by crystallization by pinhole diffusion from a 50:50 mixture of diethyl ether and dichloromethane. For full crystallographic data, request report #JMS0435 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 2974 (w), 2920 (w), 2876 (m), 1711 (s), 1575 (s), 1502 (w), 1470 (w), 1434 (w), 1381 (w), 1337 (s), 1303 (m), 1285 (m), 1262 (m), 1184 (s), 1161 (s), 1141 (s), 1113 (s), 1075 (m), 1027 (w), 987 (m), 967 (m), 912 (m), 845 (w), 796 (w), 740 (m); ^{1}H NMR (500 MHz, Dichloromethane-d_2) δ 3.85 (app. td, 1H, J_{H1-H2} = 7.6 Hz, $J_{H1-H7eq}$ = 8.5 Hz, $J_{H1-H7ax}$ = 4.2 Hz, H_1), 3.55 (dd, 1H, J_{H2-H3} = 7.6 Hz, J_{H3-H4} = 3.7 Hz, H_3), 3.22 (t, 1H, J_{H1-H2} = J_{H2-H3} = 7.6 Hz, H_2), 3.06 (ddd, 1H, $J_{H7ax-H7eq}$ = 14.2 Hz, $J_{H1-H7eq}$ = 8.5 Hz, $J_{H6-H7eq}$ = 8.3 Hz, H_{7eq}), 2.77 (ddd, 1H, J_{H5-H6} = 6.6 Hz, $J_{H6-H7eq}$ = 8.3 Hz, $J_{H6-H7ax}$ = 4.7 Hz, H_6), 2.40 (m, 1H, H_4), 2.35 (dd, 1H, J_{H5-H6} = 6.6 Hz, H_{H4-H5} = 5.0 Hz, H_5), 2.17 (dt, 1H, $J_{H7ax-H7eq}$ = 14.2 Hz, $J_{H6-H7ax}$ = 4.7 Hz, $J_{H1-H7ax}$ = 4.2 Hz, H_{7ax}), 1.82 (s, 15H, $CpMe_5$), 1.47 (d, 3H, J_{H4-CH3} = 6.9 Hz, C_4-CH_3); ^{13}C NMR (125 MHz, Dichloromethane-d_2) δ 98.1 ($\underline{C_5}Me_5$), 92.5 (C_2), 55.9 (C_5), 52.4 (C_3), 46.0 (C_6), 44.4 (C_1), 27.3 (C_4), 22.1 (C_7), 19.7 (C_4-CH_3), 9.9 ($C_5\underline{Me_5}$); HMQC (500 MHz, Dichloromethane-d_2) δ 92.5 ↔ δ 3.22; δ 55.9 ↔ δ 2.35; δ 52.4 ↔ δ 3.55; δ 46.0 ↔ δ 2.77; δ 44.4 ↔ δ 3.85; δ 27.3 ↔ δ 2.40; δ 22.1 ↔ δ 3.06, δ 2.17; δ 19.7 ↔ δ 1.47; δ 9.9 ↔ δ 1.82. HMBC (500 MHz, Dichloromethane-d_2) δ 92.5 ↔ δ 3.06; δ 55.9 ↔ δ 3.06, δ 1.47; δ 52.4 ↔ δ 1.47; δ 46.0 ↔ δ 3.06, δ 2.35, δ 2.17; δ 44.4 ↔ δ 3.55, δ 3.22, δ 3.06, δ 2.17; δ 27.3 ↔ δ 3.22, δ 2.77, δ 1.47; δ 22.1 ↔ δ 3.22, δ 2.77, δ 2.35; δ 19.7 ↔ δ 2.35. Analysis calculated for $C_{18}H_{26}CoPF_6$: C, 48.44; H, 5.87; found: C, 48.18; H, 5.91.



458 **472**

Cp*Co(III) 7-methyl-cycloheptadienyl hexafluorophosphate (472): An NMR tube was charged with a solution of **458** (10.7 mg, 0.161 mmol, >95% pure) in dichloromethane-d_2 (~ 750 μL). The tube was tightly sealed, and stored at room temperature for 4 d, at which point ^{1}H NMR analysis revealed a 12% conversion of **458** to η^5-cycloheptadienyl complex **472**. The NMR tube was then heated at 60 °C for 17 h, at which point the conversion was determined by ^{1}H NMR to be >98% complete. Upon removal of solvent *in vacuo*, **472** (10.7 mg, 0.161 mmol, 100%, >95% pure) was recovered as an orange-red solid. As complex **472** had been previously prepared and characterized as the trifluoromethanesulfonate salt by Dzwiniel,[17] no further purification or characterization was undertaken.

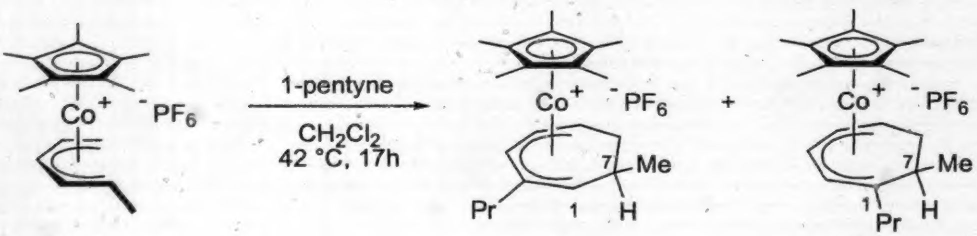


430 **480**

Cp*Co(III) 1,2,7-trimethylcycloheptadienyl hexafluorophosphate (480):

A glass bomb was charged with a solution of **430** (67.8 mg, 0.161 mmol) in dichloromethane (~ 4mL). Argon was streamed through the solution for several minutes, prior to the injection via syringe of 2-butyne (75 µL, ~0.96 mmol). The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo*, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high-vacuum, analytically pure **480** (75.6 mg, 0.159 mmol, 99%) was obtained; efforts to grow X-ray quality crystals proved fruitless. IR (microscope, cm^{-1}) 2971 (s), 2912 (s), 2826 (s), 1675 (w), 1576 (w), 1436 (s), 1381 (s), 1325 (m), 1298 (m), 1230 (w), 1206 (w), 1195 (m), 1160 (w), 1118 (w), 1074 (m), 1029 (s), 961 (m), 933 (w), 904 (m), 874 (m), 843 (m), 776 (m), 740 (m), 677 (m); ^1H NMR (400 MHz, Chloroform-d_3) δ 6.46 (d, 1H, J_{H3-H4} = 7.4 Hz, H_3), 4.58 (ddd, 1H, J_{H3-H4} = 7.4 Hz, J_{H4-H5} = 9.0 Hz, $J_{H4-H6eq}$ = 1.2 Hz, H_4), 4.29 (ddd, 1H, J_{H4-H5} = 9.0 Hz, $J_{H5-H6ax}$ = 3.0 Hz, $J_{H5-H6eq}$ = 4.4 Hz, H_5), 2.49 (ddd, 1H, [illegible]$_{H6ax}$ = 3.0 Hz, $J_{H6ax-H6eq}$ = 16.8 Hz, $J_{H6ax-H7}$ = 11.6 Hz, H_{6ax}), 2.20 (s, 3H, C_2-CH_3), 2.17 (ddt, 1H, $J_{H4-H6eq}$ = 1.2 Hz , $J_{H5-H6eq}$ = 4.4 Hz, $J_{H6ax-H6eq}$ = 16.8 Hz, $J_{H6eq-H7}$ = 4.4 Hz, H_{6eq}), 1.74 (s, 15H, $CpMe_5$), 1.28 (s, 3H, C_1-CH_3), 0.86 (d, 3H, J_{H7-CH3} = 6.8 Hz, C_7-CH_3), 0.27 (m, 1H, J_{H7-CH3} = 6.8 Hz, H_7); ^1H-

^{1}H GCOSY (400 MHz, Chloroform-d_3) δ 6.46 ↔ δ 4.58, δ 2.20; δ 4.58 ↔ δ 4.29, δ 2.17; δ 4.29 ↔ δ 2.49, δ 2.17; δ 2.49 ↔ δ 2.17, δ 0.27; δ 2.17 ↔ δ 0.27; δ 0.86 ↔ δ 0.27; ^{13}C NMR (100 MHz, Chloroform-d_3) δ 108.4 (C_2), 102.2 (C_1), 98.8(C_3), 97.5 ($\underline{\mathrm{C}_5}\mathrm{Me}_5$), 96.4 ($C_4$), 87.1 ($C_5$), 50.3 ($C_6$), 36.6 ($C_7$), 19.5 ($C_1$-$CH_3$), 17.3 ($C_2$-$CH_3$), 16.0 ($C_7$-$CH_3$), 9.0 ($\mathrm{C}_5\underline{\mathrm{Me}_5}$); HMQC (400 MHz, Chloroform-d_3) δ 98.8 ↔ δ 6.46; δ 96.4 ↔ δ 4.58; δ 87.1 ↔ δ 4.29; δ 50.3 ↔ δ 2.49, δ 2.17; δ 19.4 ↔ δ 1.28; δ 17.3 ↔ δ 2.20; δ 16.0 ↔ δ 0.86; δ 9.0 ↔ δ 1.74. HMBC (400 MHz, Chloroform-d_3) δ 108.4 ↔ δ 6.46, δ 4.58, δ 2.20, δ 1.28; δ 102.2 ↔ δ 6.46, δ 2.20, δ 1.28, δ 0.86; δ 98.8 ↔ δ 4.29, δ 2.20; δ 97.5 ↔ δ1.74; δ 96.4 ↔ δ 6.46, δ 2.49; δ 87.1 ↔ δ 6.46, δ 4.58, δ 2.49, δ 0.86; δ 50.3 ↔ δ 4.58, δ 0.86; δ 36.6 ↔ δ 4.29, δ 2.49, δ 1.28, δ 0.86; δ 17.3 ↔ δ 6.46; δ 16.0 ↔ δ 1.28. Analysis calculated for $C_{20}H_{30}CoPF_6$: C, 50.64; H, 6.37; found: C, 50.53; H, 6.53. Electrospray high-resolution mass spectrometry; mass calculated for $C_{20}H_{30}Co$: 329.16740; found: 329.16741.



430

490
major (69%)

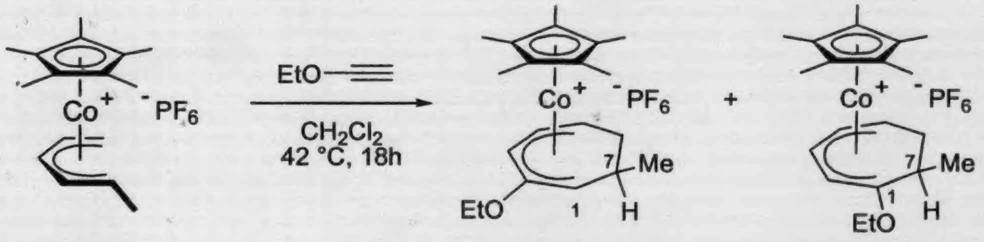
489
minor (31%)

Cp*Co(III) 7-methyl-2-propyl-cycloheptadienyl hexafluorophosphate (490) and Cp*Co(III) 7-methyl-1-propyl-cycloheptadienyl hexafluorophosphate (489):

A glass bomb was charged with a solution of **430** (17.8 mg, 0.0424 mmol) in freshly distilled dichloromethane (~ 1mL). 1-Pentyne (25 μL, ~0.25 mmol) was added via syringe, the bomb was sealed, and the solution was maintained at 42 °C for 17 h. The solvent was removed *in vacuo*, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high-vacuum, a 69:31 mixture (as determined by ^{1}H NMR integration) of **490** and **489** (18.8 mg, 0.0385 mmol, 91%) was obtained. Although pinhole diffusion of diethyl ether into dichloromethane afforded analytically pure material, efforts to grow X-ray quality crystals proved fruitless. The product was characterized as a mixture, although the NMR data for **489** and **490** are presented individually. IR (microscope, cm^{-1}) 2967 (s), 2934 (s), 2874 (s), 1578 (w), 1464 (s), 1384 (s), 1335 (w), 1316 (w), 1306 (w), 1241 (w), 1203 (w), 1156 (w), 1083 (m), 1026 (m), 968 (w), 936 (m), 906 (m), 857 (s), 775 (m), 741 (m), 724 (m); ^{1}H NMR (600 MHz, Chloroform-d$_3$) Major Isomer **490**: δ 6.38 (dd, 1H, J_{H3-H4} = 7.0 Hz, J_{H1-H3} = 1.6 Hz, H_3), 4.96 (ddm, 1H, J_{H3-H4} = 7.0 Hz, J_{H4-H5} = 9.1 Hz, H_4), 4.40 (ddd, 1H, J_{H4-H5} =

9.1 Hz, $J_{H5\text{-}H6ax}$ = 4.8 Hz, $J_{H5\text{-}H6eq}$ = 3.3 Hz, H_5), 3.61 (dd, 1H, $J_{H1\text{-}H7}$ = 3.5 Hz, $J_{H1\text{-}H3}$ = 1.6 Hz, H_1), 2.51 (m, 1H, $\text{-C}\underline{\text{H}}_2\text{CH}_2\text{CH}_3$), 2.27 (ddd, 1H, $J_{H5\text{-}H6ax}$ = 4.8 Hz, $J_{H6ax\text{-}H6eq}$ = 16.7 Hz, $J_{H6ax\text{-}H7}$ = 8.8 Hz, H_{6ax}), 1.95 (m, 1H, $J_{H5\text{-}H6eq}$ = 3.3 Hz, $J_{H6ax\text{-}H6eq}$ = 16.7 Hz, H_{6eq}), 1.84 (s, 15H, CpMe$_5$), 1.8 – 1.7 (m, 3H, $\text{-C}\underline{\text{H}}_2\text{CH}_2\text{CH}_3$ (1H) and $\text{-CH}_2\text{C}\underline{\text{H}}_2\text{CH}_3$ (2H)), 1.08 (d, 3H, $J_{H7\text{-}CH3}$ = 6.8 Hz, $C_7\text{-CH}_3$), 1.00 (t, 3H, J = 7.1 Hz, $\text{-CH}_2\text{CH}_2\text{C}\underline{\text{H}}_3$), 0.85 (m, 1H, $J_{H7\text{-}CH3}$ = 6.8 Hz, H_7); ^{1}H NMR (600 MHz, Chloroform-d$_3$) Minor Isomer **489**: δ 6.52 (app. td, 1H, $J_{H2\text{-}H3}$ = 7.0 Hz, $J_{H3\text{-}H4}$ = 7.2 Hz, $J_{H3\text{-}H5}$ = 1.2 Hz, H_3), 5.19 (app. t, 1H, $J_{H3\text{-}H4}$ = 7.2 Hz, $J_{H4\text{-}H5}$ = 6.5 Hz, H_4), 4.93 (d, 1H, $J_{H2\text{-}H3}$ = 7.0 Hz, H_2), 4.28 (dddd, 1H, $J_{H4\text{-}H5}$ = 6.5 Hz, $J_{H5\text{-}H6ax}$ = 7.5 Hz, $J_{H5\text{-}H6eq}$ = 5.0 Hz, $J_{H3\text{-}H5}$ = 1.2 Hz, H_5), 2.38 (ddd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 10.0 Hz, J_{vic} = 4.6 Hz, $\text{-C}\underline{\text{H}}_2\text{CH}_2\text{CH}_3$), 1.94 (m, 1H, $J_{H7\text{-}CH3}$ = 6.8 Hz, H_7), 1.82 (s, 15H, CpMe$_5$), 1.7 (m, 1H, $\text{-CH}_2\text{C}\underline{\text{H}}_2\text{CH}_3$), 1.51 (ddd, 1H, $J_{H5\text{-}H6ax}$ = 7.5 Hz, $J_{H6ax\text{-}H6eq}$ = 13.7 Hz, $J_{H6ax\text{-}H7}$ = 2.8 Hz, H_{6ax}), 1.45 (m, 1H, $\text{-CH}_2\text{C}\underline{\text{H}}_2\text{CH}_3$), 1.41 (d, 3H, $J_{H7\text{-}CH3}$ = 6.8 Hz, $C_7\text{-CH}_3$), 1.34 (ddd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 10.6 Hz, J_{vic} = 6.2 Hz, $\text{-C}\underline{\text{H}}_2\text{CH}_2\text{CH}_3$), 0.98 (t, 3H, J = 7.3 Hz, $\text{-CH}_2\text{CH}_2\text{C}\underline{\text{H}}_3$), 0.49 (m, 1H, $J_{H5\text{-}H6eq}$ = 5.0 Hz, $J_{H6ax\text{-}H6eq}$ = 13.7 Hz, H_{6eq}); ^{1}H-^{1}H GCOSY (500 MHz, Chloroform-d$_3$) Major Isomer **490**: δ 6.38 ↔ δ 4.96, δ 4.40, δ 3.61; δ 4.96 ↔ δ 4.40, δ 1.95; δ 4.40 ↔ δ 2.27, δ 1.95; δ 3.61 ↔ δ 0.85; δ 2.51 ↔ δ 1.8, δ 1.7, δ 1.00; δ 2.27 ↔ δ 1.95, δ 0.85; δ 1.95 ↔ δ 0.85; δ 1.8 ↔ δ 1.7, δ 1.00; δ 1.7 ↔ δ 1.00; δ 1.08 ↔ δ 0.85; ^{1}H-^{1}H GCOSY (500 MHz, Chloroform-d$_3$) Minor Isomer **489**: δ 6.52 ↔ δ 5.19, δ 4.93, δ 4.28; δ 5.19 ↔ δ 4.93, δ 4.28, δ 0.49; δ 4.28 ↔ δ 1.51, δ 0.49; δ 2.38 ↔ δ 1.7, δ 1.45, δ 1.34; δ 1.94 ↔ δ 1.51, δ 1.41, δ 0.49; δ 1.7 ↔ δ 1.45, δ 1.34, δ 0.98; δ 1.51 ↔ δ 0.49; δ 1.45 ↔ δ 1.34, δ 0.98; ^{13}C NMR (125 MHz, Chloroform-d$_3$) Major Isomer **490**: δ 113.5 (C_2), 99.0 (C_3), 98.5 ($\underline{\text{C}}_5\text{Me}_5$), 97.6 ($C_4$), 91.1 ($C_5$), 90.4 ($C_1$), 46.3 ($C_6$), 38.1 ($\text{-}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_3$), 36.0 ($C_7$), 25.6 (-

$CH_2\underline{C}H_2CH_3$), 22.4 (C_7-CH_3), 13.5 (-CH_2-$CH_2\underline{C}H_3$), 9.7 ($C_5\underline{Me_5}$); ^{13}C NMR (125 MHz, Chloroform-d_3) Minor Isomer **489**: δ 116.4 (C_1), 99.8 (C_4), 98.2 (C_2), 97.9 ($\underline{C_5}Me_5$), 97.2 (C_3), 85.5 (C_5), 46.2 (C_7), 41.0 (-$\underline{C}H_2CH_2CH_3$), 36.2 (C_6), 23.2 (-$CH_2\underline{C}H_2CH_3$), 22.0 (C_7-CH_3), 14.1 (-CH_2-$CH_2\underline{C}H_3$), 9.6 ($C_5\underline{Me_5}$); HMQC (500 MHz, Chloroform-d_3) Major Isomer **490**: δ 99.0 ↔ δ 6.38; δ 97.6 ↔ δ 4.96; δ 91.1 ↔ δ 4.40; δ 90.4 ↔ δ 3.61; δ 46.3 ↔ δ 2.27, δ 1.95; δ 38.1 ↔ δ 2.51, δ 1.7; δ 36.0 ↔ δ 0.85; δ 25.6 ↔ δ 1.8, δ 1.7; δ 22.4 ↔ δ 1.08; δ 13.5 ↔ δ 1.00; δ 9.7 ↔ δ 1.84; HMQC (500 MHz, Chloroform-d_3) Minor Isomer **489**: δ 99.8 ↔ δ 5.19; δ 98.2 ↔ δ 4.93; δ 97.2 ↔ δ 6.52; δ 85.5 ↔ δ 4.28; δ 46.2 ↔ δ 1.94; δ 41.0 ↔ δ 2.38, δ 1.34; δ 36.2 ↔ δ 1.51, δ 0.49; δ 23.2 ↔ δ 1.7, δ 1.45; δ 22.0 ↔ δ 1.41; δ 14.1 ↔ δ 0.98; δ 9.6 ↔ δ 1.82. Analysis calculated for $C_{21}H_{32}CoPF_6$: C, 51.65; H, 6.60; found: C, 51.30; H, 6.35. Electrospray high-resolution mass spectrometry; mass calculated for $C_{21}H_{32}Co$: 343.18305; found: 343.18330.

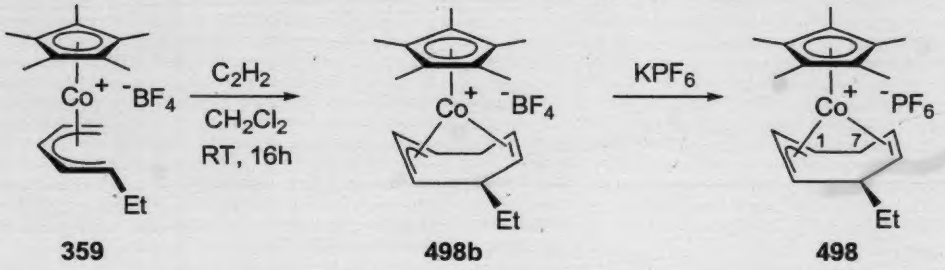


430 **492** major (64%) **491** minor (36%)

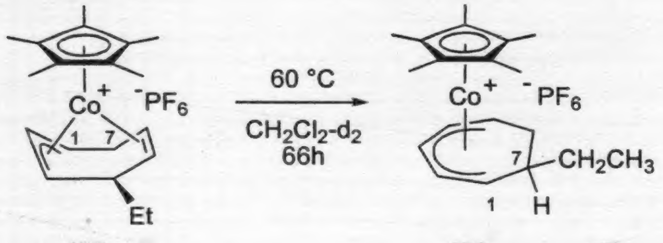
Cp*Co(III) 7-methyl-2-ethoxy-cycloheptadienyl hexafluorophosphate (492) and Cp*Co(III) 7-methyl-1-ethoxy-cycloheptadienyl hexafluorophosphate (491):

A glass bomb was charged with a solution of **430** (29.2 mg, 0.0695 mmol) in freshly distilled dichloromethane (~ 1 mL). Ethoxyacetylene (50 μL, 40% solution in hexanes, ~0.29 mmol) was added via syringe, the bomb was sealed, and the solution was maintained at 42 °C for 18h. The solvent was removed in vacuo, and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent and subsequent drying under high vacuum, a 64:36 mixture (as determined by ^{1}H NMR integration) of **492** and **491** (27.9 mg, 0.0569 mmol, 82%) was obtained. Efforts to grow X-ray quality crystals proved fruitless. The product was characterized as a mixture, although the NMR data for **491** and **492** is presented individually. IR (microscope, cm^{-1}) 2979 (m), 2927 (m), 1471 (m), 1381 (m), 1326 (w), 1296 (w), 1234 (w), 1199 (m), 1176 (m), 1152 (w), 1103 (w), 1077 (w), 1026 (m), 875 (m), 838 (s), 739 (w); ^{1}H NMR (400 MHz, Chloroform-d) Major Isomer **492**: δ 6.24 (dd, 1H, $J_{H3\text{-}H4}$ = 7.2 Hz, $J_{H1\text{-}H3}$ = 3.2 Hz, H_3), 5.07 (ddd, 1H, $J_{H3\text{-}H4}$ = 7.2 Hz, $J_{H4\text{-}H5}$ = 9.0 Hz, $J_{H4\text{-}H6eq}$ = 1.4 Hz, H_4), 4.31 (ddd, 1H, $J_{H4\text{-}H5}$ = 9.0 Hz, $J_{H5\text{-}H6ax}$ = 5.5 Hz, $J_{H5\text{-}H6eq}$ = 3.3 Hz, H_5), 4.12 (dq, 1H, J_{gem} = 9.6 Hz, J_{vic} = 7.0 Hz, $-OC\underline{H}_2CH_3$), 3.97 (dq, 1H, J_{gem} = 9.6 Hz, J_{vic} = 7.0 Hz, $-OC\underline{H}_2CH_3$), 3.75 (dd, 1H, $J_{H1\text{-}H7}$ = 3.8 Hz, $J_{H1\text{-}H3}$ = 3.2 Hz, H_1), 2.03 (ddd, 1H, $J_{H5\text{-}H6ax}$ = 5.5 Hz, $J_{H6ax\text{-}H6eq}$ = 15.9 Hz, $J_{H6ax\text{-}H7}$ = 6.8 Hz, H_{6ax}), 1.82 (s, 15H, $CpMe_5$), 1.64 (m, 1H, $J_{H5\text{-}H6eq}$ = 3.3 Hz, $J_{H6ax\text{-}H6eq}$ = 15.9 Hz, H_{6eq}), 1.40 (t, 3H, J = 7.0 Hz, $-OCH_2C\underline{H}_3$), 1.15 (d, 3H, $J_{H7\text{-}CH3}$ = 5.4 Hz, $C_7\text{-}CH_3$), 1.11 (m, 1H, $J_{H1\text{-}H7}$ = 3.8 Hz, $J_{H7\text{-}CH3}$ = 5.4 Hz, $J_{H6ax\text{-}H7}$ = 6.8 Hz, H_7); ^{1}H NMR (400 MHz, Chloroform-d) Minor Isomer **491**: δ 6.40 (t_{app}d, 1H, $J_{H2\text{-}H3}$ = 6.9 Hz, $J_{H3\text{-}H4}$ = 7.6 Hz, $J_{H3\text{-}H5}$ = 1.0 Hz, H_3), 4.87 (d, 1H, $J_{H2\text{-}H3}$ = 6.9 Hz, H_2), 4.79 (ddm, 1H, $J_{H3\text{-}H4}$ = 7.6 Hz, $J_{H4\text{-}H5}$ = 6.4 Hz, H_4), 4.04 (t_{app}dd, 1H, $J_{H4\text{-}H5}$ = 6.4 Hz, $J_{H5\text{-}H6ax}$ = 8.0 Hz, $J_{H5\text{-}H6eq}$ = 4.7 Hz, $J_{H3\text{-}H5}$ = 1.0 Hz, H_5), 1.95 (m, 1H, $J_{H5\text{-}H6ax}$ = 8.0 Hz, $J_{H6ax\text{-}H6eq}$ = 15.2 Hz, H_{6ax}), 1.77 (s, 15H, $CpMe_5$), 1.67 (m, 1H, $J_{H7\text{-}CH3}$ = 6.8 Hz, H_7), 1.40 (t, 3H, J = 7.0 Hz, $-OCH_2C\underline{H}_3$), 1.32 (td, 1H, $J_{H5\text{-}H6eq}$ = 4.7

Hz, $J_{H6eq\text{-}H7}$ = 4.7 Hz, $J_{H6ax\text{-}H6eq}$ = 15.2 Hz, H_{6eq}), 1.17 (d, 3H, $J_{H7\text{-}CH3}$ = 6.8 Hz, C_7-CH_3); ^{1}H-^{1}H GCOSY (400 MHz, Chloroform-d) Major Isomer **492**: δ 6.24 ↔ δ 5.07, δ 3.75; δ 5.07 ↔ δ 4.31; δ 4.31 ↔ δ 2.03, δ 1.64; δ 4.12 ↔ δ 3.97, δ 1.40; δ 3.97 ↔ δ 1.40; δ 3.75 ↔ δ 1.11; δ 2.03 ↔ δ 1.64, δ 1.11; δ 1.64 ↔ δ 1.11; δ 1.15 ↔ δ 1.11; ^{1}H-^{1}H GCOSY (400 MHz, Chloroform-d) Minor Isomer **491**: δ 6.40 ↔ δ 4.87, δ 4.79; δ 4.79 ↔ δ 4.04; δ 4.04 ↔ δ 1.95, δ 1.32; δ 3.81 ↔ δ 3.79, δ 1.40; δ 3.79 ↔ δ 1.40; δ 1.95 ↔ δ 1.67, δ 1.32; δ 1.67 ↔ δ 1.32, δ 1.17; δ 1.32 ↔ δ 1.17; ^{13}C NMR (100 MHz, Chloroform-d) Major Isomer **492**: δ 139.7 (C_2), 98.3 ($\underline{C}_5Me_5$), 94.8 (C_4), 89.0 (C_5), 84.8 (C_3), 77.2 (C_1), 67.3 ($-O\underline{C}H_2CH_3$), 43.6 (C_6), 36.1 (C_7), 22.7 (C_7-CH_3), 14.5 ($-OCH_2\underline{C}H_3$), 9.9 ($C_5\underline{Me}_5$); ^{13}C NMR (100 MHz, Chloroform-d) Minor Isomer **491**: δ 151.2 (C_1), 97.0 ($\underline{C}_5Me_5$), 95.6 (C_4), 91.8 (C_3), 79.5 (C_5), 78.2 (C_2), 66.2 ($-O\underline{C}H_2CH_3$), 42.4 (C_7), 41.2 (C_6), 18.2 (C_7-CH_3), 14.3 ($-OCH_2\underline{C}H_3$), 9.4 ($C_5\underline{Me}_5$); HMQC (400 MHz, Chloroform-d) Major Isomer **492**: δ 94.8 ↔ δ 5.07; δ 89.0 ↔ δ 4.31; δ 84.8 ↔ δ 6.24; δ 77.2 ↔ δ 3.75; δ 67.3 ↔ δ 4.12, δ 3.97; δ 43.6 ↔ δ 2.03, δ 1.64; δ 36.1 ↔ δ 1.11; δ 22.7 ↔ δ 1.15; δ 14.5 ↔ δ 1.40; δ 9.9 ↔ δ 1.82; HMQC (400 MHz, Chloroform-d) Minor Isomer **491**: δ 95.6 ↔ δ 4.79; δ 91.8 ↔ δ 6.40; δ 79.5 ↔ δ 4.04; δ 78.2 ↔ δ 4.87; δ 66.2 ↔ δ 3.81, δ 3.79; δ 42.9 ↔ δ 1.67; δ 41.2 ↔ δ 1.95, δ 1.32; δ 18.2 ↔ δ 1.17; δ 14.3 ↔ δ 1.40; δ 9.4 ↔ δ 1.77. Analysis calculated for $C_{20}H_{30}CoOPF_6$: C, 48.99; H, 6.17; found: C, 50.15; H, 6.24. Electrospray high-resolution mass spectrometry; mass calculated for $C_{20}H_{30}CoO$: 345.16231; found: 345.16234.



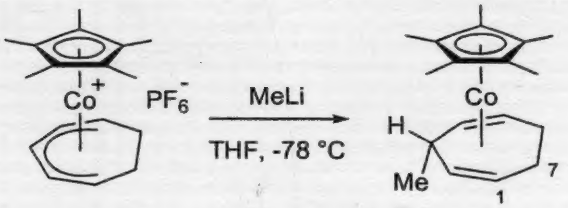
Cp*Co(III) η^3,η^2-4-ethylcycloheptadienyl hexafluorophosphate (498): A test tube was charged with a solution of **359** (47.9 mg, 0.127 mmol) in freshly distilled dichloromethane (5 mL). The tube was fitted with a septum, and acetylene was streamed through the solution for ~15 minutes, to ensure saturation. The solution was maintained at room temperature for 18 h, before the removal of solvent by rotary evaporation. The orange-red residue was chromatographed on silica gel with a 4% methanol in dichloromethane mixture, affording a red gum (46.6 mg, 0.116 mmol, 91%) which was comprised primarily of **498b**, but contained traces (less than 5% each by ^{1}H NMR integration) of minor impurities. **498b** was completely dissolved in water (~ 3 mL), and treated with saturated aqueous KPF_6 (5 mL). The red precipate was collected by filtration and chromatographed on silica gel with a 4% methanol in dichloromethane mixture to furnish **498** as a red powder (41.3 mg, 0.0897 mmol, 77% from **498b**). Crystals of analytical purity and suitable for X-ray diffraction study were grown from a 50:50 mixture of diethyl ether and dichloromethane at -80 °C. For full crystallographic data, request report #JMS0439 from the X-Ray Crystallography Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3003 (w), 2968 (m), 2928 (m), 2879 (w), 1470 (m), 1460 (m), 1388 (m), 1379 (m), 1308 (w), 1290 (w), 1236 (w), 1073 (w), 1028 (w), 991 (w), 940 (w), 907 (w), 891 (w), 877 (m), 843 (s), 806 (m), 777 (w); ^{1}H NMR (400 MHz, Dichloromethane-d_2) δ 3.84 (dtm, 1H, $J_{H1\text{-}H2}$ = 7.6 Hz, $J_{H1\text{-}H7eq}$ = 8.4 Hz, $J_{H1\text{-}H7ax}$ = 4.2 Hz, H_1), 3.61 (dd, 1H, $J_{H2\text{-}H3}$ = 7.6 Hz, $J_{H3\text{-}H4}$ = 3.6 Hz, H_3), 3.23 (tm, 1H, $J_{H1\text{-}H2}$ = $J_{H2\text{-}H3}$ = 7.6 Hz, H_2), 3.07 (dtm, 1H, $J_{H7ax\text{-}H7eq}$ = 14.2 Hz, $J_{H1\text{-}H7eq}$ = 8.4 Hz, $J_{H6\text{-}H7eq}$ = 8.4 Hz, H_{7eq}), 2.79 (dt$_{app}$, 1H, $J_{H5\text{-}H6}$ = 6.6 Hz, $J_{H6\text{-}H7eq}$ = 8.4 Hz, $J_{H6\text{-}H7ax}$ = 4.7 Hz, H_6), 2.39 (dd, 1H, $J_{H5\text{-}H6}$ = 6.6 Hz, $J_{H4\text{-}H5}$ = 4.6 Hz, H_5), 2.19 (app. dt, 1H, $J_{H1\text{-}H7ax}$ = 4.2 Hz, $J_{H7ax\text{-}H7eq}$ = 14.2 Hz, $J_{H6\text{-}H7ax}$ = 4.7 Hz, H_{7ax}), 2.16 (m, 1H, H_4), 1.85 (m, 2H, $-C\underline{H}_2CH_3$), 1.81 (s, 15H, $CpMe_5$), 1.04 (t, 3H, $J_{CH2\text{-}CH3}$ = 7.4 Hz, $-CH_2C\underline{H}_3$); ^{1}H-^{1}H GCOSY (500 MHz, Dichloromethane-d_2) δ 3.84 ↔ δ 3.23, δ 3.07, δ 2.19; δ 3.61 ↔ δ 3.23, δ 2.16; δ 3.23 ↔ δ 2.19; δ 3.07 ↔ δ 2.79, δ 2.39, δ 2.19; δ 2.79 ↔ δ 2.39, δ 2.19; δ 2.39 ↔ δ 2.16; δ 2.16 ↔ δ 1.85; δ 1.85 ↔ δ 1.04; ^{13}C NMR (100 MHz, Dichloromethane-d_2) δ 98.1 ($\underline{C}_5Me_5$), 92.5 (C_2), 54.7 (C_5), 50.9 (C_3), 46.2 (C_6), 44.5 (C_1), 34.1 (C_4), 27.5 ($-\underline{C}H_2CH_3$), 22.1 (C_7), 10.9 ($-CH_2\underline{C}H_3$), 9.9 ($C_5\underline{Me}_5$); HMQC (400 MHz, Dichloromethane-d_2) δ 92.5 ↔ δ 3.23; δ 54.7 ↔ δ 2.39; δ 50.9 ↔ δ 3.61; δ 46.2 ↔ δ 2.79; δ 44.5 ↔ δ 3.84; δ 27.5 ↔ δ 1.85; δ 22.1 ↔ δ 3.07, δ 2.19; δ 10.9 ↔ δ 1.04; δ 9.9 ↔ δ 1.81. HMBC (500 MHz, Dichloromethane-d_2) δ 98.1 ↔ δ 1.81; δ 92.5 ↔ δ 3.07; δ 54.7 ↔ δ 3.07, δ 2.79, δ 1.85; δ 50.9 ↔ δ 3.84, δ 3.23, δ 1.85; δ 46.2 ↔ δ 3.07, δ 2.39, δ 2.19; δ 44.5 ↔ δ 3.61, δ 3.23, δ 3.07; δ 27.5 ↔ δ 3.61, δ 2.39, δ 1.04; δ 22.1 ↔ δ 3.23, δ 2.79, δ 2.39; δ 10.9 ↔ δ 1.85. Analysis calculated for $C_{19}H_{28}CoPF_6$: C, 49.58; H, 6.13; found: C, 49.47; H, 5.98.



498 **499**

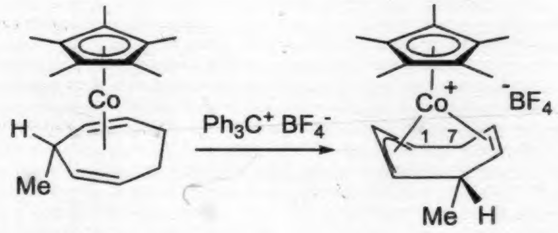
Cp*Co(III) 7-ethyl-cycloheptadienyl hexafluorophosphate (499): An NMR tube was charged with a solution of **498** (11.1 mg, 0.161 mmol) in dichloromethane-d_2 (~ 750 µL). The tube was tightly sealed, and the reaction was heated at 60 °C for 1h, at which point ^{1}H NMR interrogation revealed an approximately 8% conversion to η^5-cycloheptadienyl product **499**. Heating at 60 °C was resumed; NMR analysis revealed an approximately 75% conversion after 19 h, and complete conversion after 66 h. The deuterated solvent was removed *in vacuo*, and the red-orange residue was chromatographed on silica gel with 3% methanol/dichloromethane, furnishing **499** as an analytically pure powder (11.0 mg, 0.160 mol, 99%) after drying under high-vacuum. IR (microscope, cm^{-1}) 2968 (m), 2918 (m), 2877 (m), 1496 (m), 1463 (m), 1434 (m), 1406 (s), 1380 (m), 1345 (w), 1313 (w), 1138 (w), 1076 (w), 1027 (m), 980 (w), 911 (w), 882 (s), 843 (s), 779 (w), 740 (w); ^{1}H NMR (400 MHz, Chloroform-d) δ 6.61 (app. td, 1H, $J_{H2-H3} = 6.7$ Hz, $J_{H3-H4} = 6.9$ Hz, $J_{H1-H3} = 1.3$ Hz, H_3), 5.26 (ddm, 1H, $J_{H1-H2} = 8.1$ Hz, $J_{H2-H3} = 6.7$ Hz, H_2), 4.90 (ddm, 1H, $J_{H3-H4} = 6.9$ Hz, $J_{H4-H5} = 9.3$ Hz, H_4), 4.33 (ddd, 1H, $J_{H4-H5} = 9.3$ Hz, $J_{H5-H6ax} = 4.3$ Hz, $J_{H5-H6eq} = 3.3$ Hz, H_5), 4.04 (ddd, 1H, $J_{H1-H2} = 8.1$ Hz, $J_{H1-H7} = 4.0$ Hz, $J_{H1-H3} = 1.3$ Hz, H_1), 2.37 (ddd, 1H, $J_{H5-H6ax} = 4.3$ Hz, $J_{H6ax-H6eq} = 16.7$ Hz, $J_{H6ax-H7} = 9.4$ Hz, H_{6ax}), 2.10 (dddd, 1H, $J_{H4-H6eq} = 1.4$ Hz , $J_{H5-H6eq} = 3.3$ Hz, $J_{H6ax-H6eq} = 16.7$ Hz, $J_{H6eq-H7} = 5.3$ Hz, H_{6eq}), 1.88 (s, 15H, $CpMe_5$), 1.46 (dp, 1H, $J_{gem} = 14.6$ Hz, $J_{CH2-CH3}$

= 7.3 Hz, $J_{H7\text{-}CH2\text{-}}$ = 7.3 Hz, -C$\underline{H}_2$CH$_3$), 1.36 (dp, 1H, J_{gem} = 14.6 Hz, $J_{CH2\text{-}CH3}$ = 7.3 Hz, $J_{H7\text{-}CH2\text{-}}$ = 7.3 Hz, -C$\underline{H}_2$CH$_3$), 0.82 (t, 3H, $J_{CH2\text{-}CH3}$ = 7.3 Hz, -CH$_2$C$\underline{H}_3$), 0.55 (m, 1H, $J_{H1\text{-}H7}$ = 4.0 Hz, $J_{H6ax\text{-}H7}$ = 9.4 Hz, $J_{H6eq\text{-}H7}$ = 5.3 Hz, $J_{H7\text{-}CH2\text{-}}$ = 7.3 Hz, H$_7$); ^{1}H-^{1}H GCOSY (400 MHz, Chloroform-d) δ 6.61 ↔ δ 5.26, δ 4.90, δ 4.04; δ 5.26 ↔ δ 4.04; δ 4.90 ↔ δ 4.33, δ 2.10; δ 4.33 ↔ δ 2.37, δ 2.10; δ 4.04 ↔ δ 0.55; δ 2.37 ↔ δ 2.10, δ 0.55; δ 2.10 ↔ δ 0.55; δ 1.46 ↔ δ 1.36, δ 0.82, δ 0.55; δ 1.36 ↔ δ 0.82, δ 0.55; ^{13}C NMR (100 MHz, Chloroform-d) δ 100.3 (C$_3$), 98.3 ($\underline{C}_5$Me$_5$), 97.7 (C$_2$), 97.6(C$_4$), 94.9 (C$_1$), 88.8 (C$_5$), 46.4 (C$_6$), 41.4 (C$_7$), 29.3 (C$_7$-$\underline{C}$H$_2$CH$_3$), 12.0 (C$_7$-CH$_2\underline{C}$H$_3$), 9.7 (C$_5\underline{Me}_5$); HMQC (400 MHz, Chloroform-d) δ 100.3 ↔ δ 6.61; δ 97.7 ↔ δ 5.26; δ 97.6 ↔ δ 4.90; δ 94.9 ↔ δ 4.04; δ 88.8 ↔ δ 4.33; δ 46.4 ↔ δ 2.37, δ 2.10; δ 41.4 ↔ δ 0.55; δ 29.3 ↔ δ 1.46, δ 1.36; δ 12.0 ↔ δ 0.82; δ 9.7 ↔ δ 1.88. HMBC (400 MHz, Chloroform-d) δ 100.3 ↔ δ 4.33, δ 4.04; δ 98.3 ↔ δ 1.88; δ 97.7 ↔ δ 6.61, δ 4.90; δ 97.6 ↔ δ 6.61, δ 5.26, 2.37; δ 94.9 ↔ δ 6.46, δ 1.46, δ 1.36; δ 88.8 ↔ δ 6.46, δ 2.37; δ 46.4 ↔ δ 4.90, δ 4.04, δ 1.46, δ 1.36; δ 41.4 ↔ δ 5.26, δ 2.37, δ 1.46, δ 1.36, δ 0.82; δ 29.3 ↔ δ 4.04, δ 2.37, δ 0.82; δ 12.0 ↔ δ 1.46, δ 1.36. Analysis calculated for $C_{19}H_{28}CoPF_6$: C, 49.58; H, 6.13; found: C, 49.52; H, 6.02. Electrospray high-resolution mass spectrometry; mass calculated for $C_{19}H_{28}Co$: 315.15188; found: 315.15175.



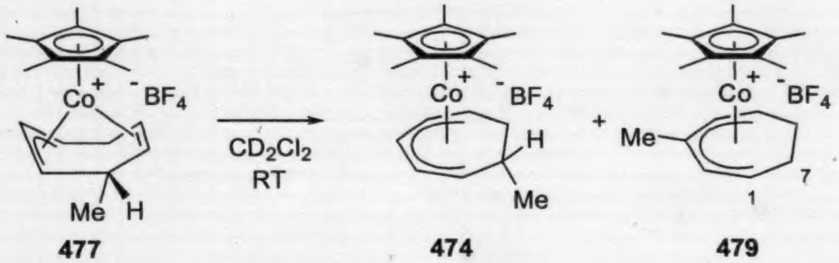
473 476

Cp*Co(I) η^4-4-methyl-1-allylcyclohepta-2,5-diene (476): This preparation was carried out in accordance with the procedure of Dzwiniel.[17] In the glove box, a Schlenk flask was charged with a solid Cp*Co(III) cycloheptadienyl complex **473** (228.2 mg, 0.5279 mmol) and then equipped with a magnetic stir-bar and septum. The flask was removed to the Schlenk line and placed under an argon atmosphere. The complex **473** was partially dissolved in distilled THF (10 mL) which was introduced to the flask via cannula. The resulting orange suspension was cooled to -78 °C, and methyl lithium (500 μL, 1.6 M in diethyl ether, 0.800 mmol) was introduced via syringe in one portion. The resulting solution was stirred at room temperature for 30 minutes, and then excess methyl lithium was quenched with methanol (1 mL). The solvent was removed *in vacuo* and the resulting orange solid was returned to the glove box. The residue was taken up in pentane, and eluted through a short plug of alumina (activity IV). The resulting yellow-orange solution was concentrated *in vacuo* to afford orange solid **476** (109.9 mg, 0.3635 mmol, 69%) upon drying. No further purification of **476** was undertaken, as **476** was to be used as-is in an effort to closely mimic Dzwiniel's preparation.[17] IR (microscope, cm^{-1}) 2987 (m), 2904 (s), 2859 (m), 2841 (m), 1443 (m), 1375 (m), 1355 (m), 1326 (w), 1315 (w), 1278 (w), 1202 (w), 1174 (w), 1027 (w), 927 (w), 756 (w); ^{1}H NMR (400 MHz, C_6D_6) δ 3.20 (sextet, 1H, $J_{H2-H3} = J_{H3-Me} = 7.4$ Hz, H_3), 2.32 (m, 2H, H_{6a}), 1.90 (m, 6H, H_1, H_2, and H_{6b}), 1.59 (s, 15H, $CpMe_5$), 0.90 (d, 3H, $J_{H3\text{-}Me} = 7.4$ Hz, C_3-$C\underline{H}_3$); ^1H-^1H GCOSY (400 MHz, C_6D_6) δ 3.20 ↔ δ 1.90, δ 0.90; δ 2.32 ↔ δ 1.90; ^{13}C NMR (100 MHz, C_6D_6) δ 90.3 ($\underline{C}_5Me_5$), 67.3 (C_1), 38.2 (C_2), 33.5 (C_3), 29.7 (C_6), 19.1 (C_3-$\underline{C}H_3$), 9.5 ($C_5\underline{Me}_5$); HMQC (400 MHz, $\underline{C}_5Me_5$) δ 67.3 ↔ δ 1.90; δ 38.2 ↔ δ 1.90; δ 33.5 ↔ δ 3.20; δ 29.7 ↔ δ 2.32, δ 1.90; δ 19.1 ↔ δ 0.90; δ 9.5 ↔ δ 1.59; HMBC (400 MHz, $\underline{C}_5Me_5$) δ 90.3 ↔ δ 1.59; δ 67.3 ↔ δ 3.20, δ 1.90; δ 38.2 ↔ δ 3.20, δ 1.90, δ 0.90; δ 33.5 ↔ δ 1.90, δ 0.90; δ 29.7 ↔ δ 2.32, δ 1.90. Analysis calculated for $C_{18}H_{27}Co$: C, 71.51; H, 9.00; found: C, 71.77; H, 8.93.



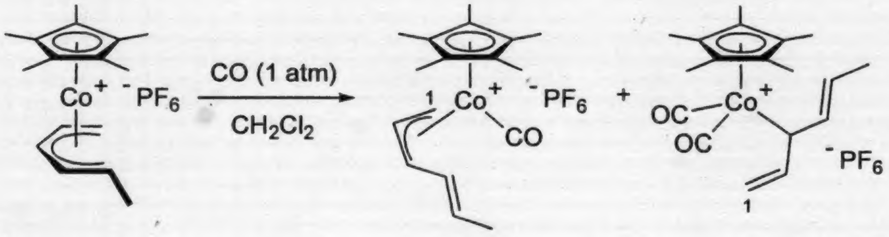
476 **477**

Cp*Co(III) η^3,η^2-4-methylcycloheptadienyl tetrafluorophosphate *endo* isomer (477): A small vial fitted with a rubber septum was charged with a solution of **476**[17] (14.9 mg, 0.0493 mmol) in CD_2Cl_2 (~800 μL), and cooled to -78 °C. This cooled solution was transferred via cannula into an NMR tube previously charged with triphenylmethyl tetrafluoroborate (18.5 mg, 0.0560 mmol) and fitted with a rubber septum. The resulting mixture was inverted several times and maintained at -78 °C for 2 hours. At the end of this time, the sample was subjected to variable temperature NMR analysis, beginning at -80 °C, and concluding at room temperature. At -80 °C, the intermediate allyl olefin complex **477** was observed to the exclusion of starting material **476**. An equivalent of triphenylmethane was also present, as well as small (less than 5% by ^{1}H NMR integration) amounts of unidentified impurities. The NMR data reported here for complex **476** was recorded at -80 °C, with the exception of the 1D ^{1}H spectrum; the ^{1}H NMR spectrum was recorded at several different temperatures, and the room temperature spectrum is reported here as it was of the highest resolution of those recorded. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.29 (app. t, 1H, J_{H2-H3} = 8.2 Hz, J_{H3-H4} = 8.8 Hz, H_3), 3.92 (app. td, 1H, J_{H1-H2} = 8.2, $J_{H1-H7eq}$ = 8.8 Hz, $J_{H1-H7ax}$ = 3.7 Hz, H_1), 3.44 (m, 1H, H_4), 3.40 (t, 1H, J_{H1-H2} = J_{H2-H3} = 8.2 Hz, H_2), 3.21 (dtm, 1H, $J_{H7eq-H7ax}$ = 14.7 Hz, $J_{H1-H7eq}$ = $J_{H6-H7eq}$ = 8.8 Hz, H_{7eq}), 2.90 (t, 1H, J_{H4-H5} = J_{H5-H6} = 7.7 Hz, H_5), 2.84 (m, 1H, H_6), 2.35 (dt, 1H, $J_{H7eq-H7ax}$ = 14.7 Hz, $J_{H1-H7ax}$ = $J_{H6-H7ax}$ = 3.7 Hz, H_{7ax}), 1.81 (s, 15H, $CpMe_5$), 0.87 (d, 1H, J_{H4-Me} = 7.3 Hz, C_4-CH_3); ^{1}H-^{1}H GCOSY (400 MHz, CD_2Cl_2) δ 4.29 ↔ δ 3.44, δ 3.40; δ 3.92 ↔ δ 3.40, δ 3.21, δ 2.35; δ 3.44 ↔ δ 2.90, δ 2.84, δ 0.87; δ 3.21 ↔ δ 2.84, δ 2.35; δ 2.90 ↔ δ 2.84; δ 2.84 ↔ δ 2.35; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 96.9 (C_2), 94.0 ($\underline{C}_5Me_5$), 58.0 (C_5), 55.6 (C_3), 50.3 (C_6), 43.1 (C_1), 30.1 (C_4), 23.2 (C_7), 21.2 (C_4-$\underline{C}H_3$), 9.4 ($C_5\underline{Me}_5$); HMQC (400 MHz, CD_2Cl_2) δ 96.9 ↔ δ 3.40; δ 58.0 ↔ δ 2.90; δ 55.6 ↔ δ 4.29; δ 50.3 ↔ δ 2.84; δ 43.1 ↔ δ 3.92; δ 30.1 ↔ δ 3.44; δ 23.2 ↔ δ 3.21, δ 2.35; δ 21.2 ↔ δ 0.87; δ 9.4 ↔ δ 1.81.



Cp*Co(III) 7-methylcycloheptadienyl tetrafluorophosphate (474) and Cp*Co(III) 3-methylcycloheptadienyl tetrafluorophosphate (479): The previous reaction mixture containing compound **477** was stored in the NMR tube at room temperature, and over the course of 48 hours the intermediate allyl olefin complex converted entirely to a mixture of two cycloheptadienyl complexes, **474** and **479**. The products were purified by silica gel chromatography (3% methanol in dichloromethane), but it was not possible to separate them from one another. After drying on the high vacuum line, isomeric compounds **474** and **479** were obtained (21.2 mg, 0.0546 mmol, 110%) as a 57:43 mixture. The greater than quantitative yield suggests either an error in weighing, or that the product mixture was not completely dried, although the elemental analysis suggests the former possibility is most likely. The compounds were characterized as a mixture, although it was possible to assign the various NMR resonances to the respective compounds on the basis of integration and careful 2D NMR analysis. Dzwiniel[17] has previously characterized complex **474**; the NMR data for **479** compound are presented here alone, although **474** and **479** were not physically separated. IR (microscope, cm^{-1}) 3063 (w), 2981 (m), 2918 (m), 2876 (m), 1811 (w), 1473 (s), 1385 (s), 1357 (w), 1309 (w), 1282 (m), 1247 (w), 1213 (w), 1182 (w), 1158 (w), 1087 (s), 919 (w), 898 (w), 872 (w), 845 (w), 793 (w), 763 (w); Compund **479**: ^{1}H NMR (400 MHz,

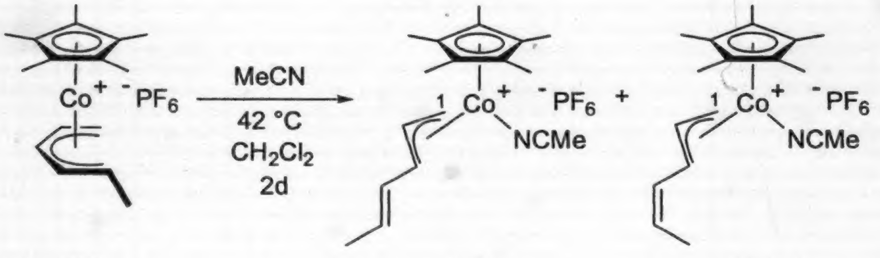
$CDCl_3$) δ 4.83 (d, 2H, J_{H1-H2} = 9.3 Hz, H_2), 4.39 (m, 2H, J_{H1-H2} = 9.3 Hz, H_1), 2.36 (s, 3H, C_3-CH_3), 2.31 (m, 2H, H_{6a} and H_{7a}), 1.84 (s, 15H, $CpMe_5$), 1.23 (m, 2H, H_{6b} and H_{7b}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.9 (C_3), 98.2 ($\underline{C_5}Me_5$), 96.2 (C_2), 91.2 (C_1), 33.6 (C_6), 20.5 (C_3-CH_3), 9.3 ($C_5\underline{Me_5}$); HMQC (400 MHz, $CDCl_3$) δ 96.2 ↔ δ 4.83; δ 91.2 ↔ δ 4.39; δ 33.6 ↔ δ 2.31, δ 1.23; δ 20.5 ↔ δ 2.36; δ 9.3 ↔ δ 1.84. Analysis calculated for $C_{18}H_{26}CoBF_4$: C, 55.70; H, 6.75; found: C, 55.97; H, 7.14. Electrospray high-resolution mass spectrometry; mass calculated for $C_{18}H_{26}Co$: 301.13610; found: 301.13604.



430 **493** **494**

Observation of Cp*Co(III)(CO) η³-hexa-2,4-dien-1-yl hexafluorophosphate (493) and Cp*Co(III)(CO)₂ η¹-hexa-2,4-dien-1-yl hexafluorophosphate (494): A glass reaction tube was charged with a solution of 1-methylpentadienyl complex **430** (22.6 mg, 0.0556 mmol) in dichloromethane (5 mL). The solution was saturated with a stream of CO, and left to stand at room temperature under a CO atmosphere. After 20 h, a small aliquot was removed and concentrated by rotary evaporation for NMR interrogation. At this point, the crude product was a mixture of **430** (~ 77%) and **493** (~ 23%). In the same way, a second aliquot was removed from the reaction after 6 days at room temperature, at which point the sample contained 3 compounds: **430** (~ 33%), **493**

(~ 56%), and the tentatively identified **494** (~ 11%). All efforts to isolate and further characterize **493** or **494** returned only starting material **430**, so only partial NMR data are reported for these products. Compound **493**: ^{1}H NMR (500 MHz, acetone-d_6) δ 6.43 (dq, 1H, $J_{H4\text{-}H5}$ = 15.3 Hz, $J_{H5\text{-}H6}$ = 7.1 Hz, H_5), 5.51 (dd, 1H, $J_{H2\text{-}H3}$ = 8.2 Hz, $J_{H3\text{-}H4}$ = 10.5 Hz, H_3), 5.10 (ddm, 1H, $J_{H4\text{-}H5}$ = 15.3 Hz, $J_{H3\text{-}H4}$ = 10.5 Hz, H_4), 4.46 (d of app. t, 1H, $J_{H1\mathit{anti}\text{-}H2}$ = 13.6 Hz, $J_{H1\mathit{syn}\text{-}H2}$ = 7.6 Hz, $J_{H2\text{-}H3}$ = 8.2 Hz, H_2), 3.90 (dm, 1H, $J_{H1\mathit{syn}\text{-}H2}$ = 7.6 Hz, $H_{1\mathit{syn}}$), 3.42 (dm, 1H, $J_{H1\mathit{anti}\text{-}H2}$ = 13.6 Hz, $H_{1\mathit{anti}}$), 2.00 (s, 15H, CpMe$_5$), 1.53 (d, 3H, $J_{H5\text{-}H6}$ = 7.1 Hz, H_6); ^{1}H-^{1}H GCOSY (500 MHz, acetone-d_6) δ 6.43 ↔ δ 5.10, δ 1.53; δ 5.51 ↔ δ 5.10, δ 4.46, δ 3.90, δ 3.42; δ 5.10 ↔ δ 1.53; δ 4.46 ↔ δ 3.90, δ 3.42; δ 3.90 ↔ δ 3.42. Compound **494**: ^{1}H NMR (500 MHz, acetone-d_6) δ 6.18 (dt, 1H, $J_{H1\mathit{trans}\text{-}H2}$ = 16.9 Hz, $J_{H1\mathit{cis}\text{-}H2}$ = $J_{H2\text{-}H3}$ = 10.3 Hz, H_2), 5.84 (d, 1H, $J_{H1\mathit{trans}\text{-}H2}$ = 16.9 Hz, $H_{1\mathit{trans}}$), 5.63 (d, 1H, $J_{H1\mathit{cis}\text{-}H2}$ = 10.3 Hz, $H_{1\mathit{cis}}$), 3.20 (m, 1H, $J_{H2\text{-}H3}$ = 10.3 Hz, H_3). All other ^{1}H NMR resonances for **494** are obscured by those of **493** or **430**.

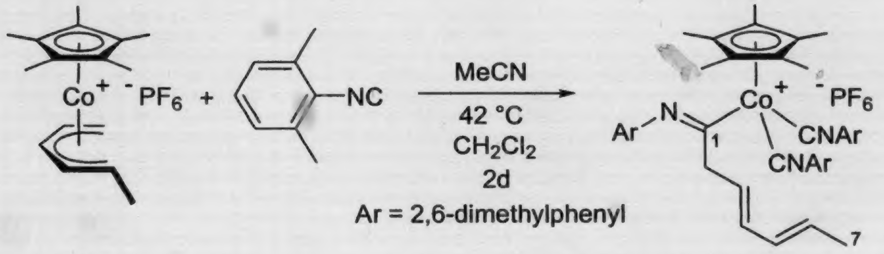


430 **495** **496**

Observation of Cp*Co(III)(MeCN) η^3-*trans*-hexa-2,4-dien-1-yl hexafluorophosphate (495) and Cp*Co(III)(MeCN) η^3-*cis*-hexa-2,4-dien-1-yl hexafluorophosphate (496): A glass bomb was charged with a solution of 1-

methylpentadienyl complex **430** (25.7 mg, 0.0633 mmol) in dichloromethane (5 mL). Acetonitrile (250 µL, 4.79 mmol) was added, the bomb was sealed, and the solution was maintained at 42 °C. After 48 h, a small aliquot was removed and concentrated by rotary evaporation for NMR interrogation revealing a mixture of **430** (~ 37%), **495** (~ 50%), and **496** (~ 13%). All efforts to isolate and further characterize **495** or **496** returned only starting material **430**, so only partial NMR data are reported for these products.

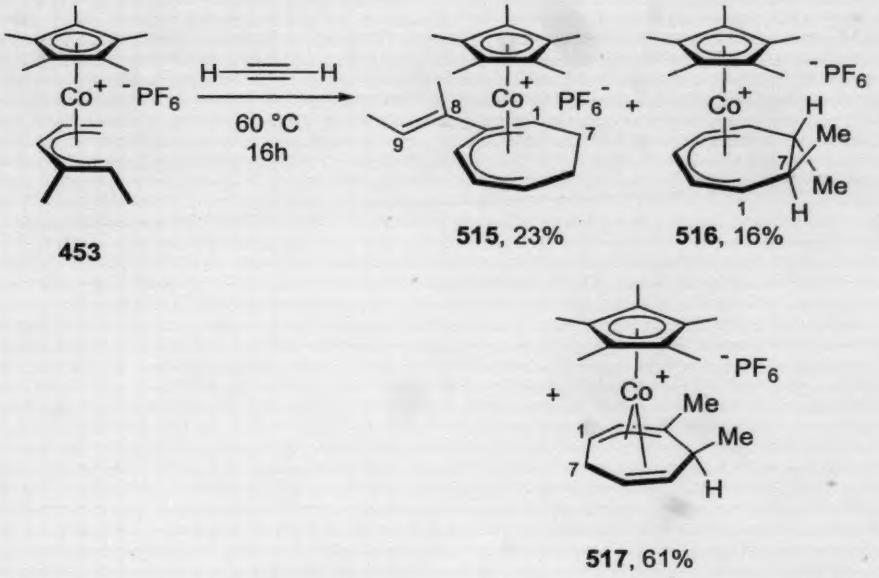
Compound **495**: ^{1}H NMR (400 MHz, acetone-d_6) δ 6.35 (dq, 1H, $J_{H4\text{-}H5}$ = 15.1 Hz, $J_{H5\text{-}H6}$ = 6.9 Hz, H_5), 6.02 (ddq, 1H, $J_{H4\text{-}H5}$ = 15.1 Hz, $J_{H3\text{-}H4}$ = 10.6 Hz, $J_{H4\text{-}H6}$ = 1.6 Hz, H_4), 4.42 (td, 1H, $J_{H1anti\text{-}H2}$ = $J_{H2\text{-}H3}$ = 12.4 Hz, $J_{H1syn\text{-}H2}$ = 7.5 Hz, H_2), 4.06 (dm, 1H, $J_{H1syn\text{-}H2}$ = 7.5 Hz, H_{1syn}), 3.42 (app. t, 1H, $J_{H2\text{-}H3}$ = 12.4 Hz, $J_{H3\text{-}H4}$ = 10.6 Hz, H_3), 2.52 (s, 3H, CH_3CN ligand), 2.24 (d, 1H, $J_{H1anti\text{-}H2}$ = 12.4 Hz, H_{1anti}), 1.70 (dd, 3H, $J_{H5\text{-}H6}$ = 6.9 Hz, $J_{H4\text{-}H6}$ = 1.6 Hz, H_6), 1.61 (s, 15H, $CpMe_5$). Compound **496**: ^{1}H NMR (400 MHz, acetone-d_6) δ 6.50 (dqd, 1H, $J_{H4\text{-}H5}$ = 10.8 Hz, $J_{H5\text{-}H6}$ = 7.2 Hz, $J_{H3\text{-}H5}$ = 1.3 Hz, H_5), 5.91 (tq, 1H, $J_{H4\text{-}H5}$ = $J_{H3\text{-}H4}$ = 10.8 Hz, $J_{H4\text{-}H6}$ = 1.7 Hz, H_4), 4.49 (td, 1H, $J_{H1\mathit{anti}\text{-}H2}$ = $J_{H2\text{-}H3}$ = 12.3 Hz, $J_{H1\mathit{syn}\text{-}H2}$ = 7.5 Hz, H_2), 4.13 (d, 1H, $J_{H1\mathit{syn}\text{-}H2}$ = 7.5 Hz, $H_{1\mathit{syn}}$), 3.47 (app. t, 1H, $J_{H2\text{-}H3}$ = 12.3 Hz, $J_{H3\text{-}H4}$ = 10.8 Hz, H_3), 2.56 (s, 3H, CH_3CN ligand), 2.33 (d, 1H, $J_{H1\mathit{anti}\text{-}H2}$ = 12.3 Hz, $H_{1\mathit{anti}}$), 1.61 (s, 15H, $CpMe_5$), 1.55 (d, 3H, $J_{H5\text{-}H6}$ = 7.2 Hz, H_6).



430

497

Reaction of Cp*Co(III) 1-methylpentadienyl hexafluorophosphate (430) with 2,6-dimethylphenyl isocyanide: A small bomb was charged with a solution of pentadienyl complex **453** (32.1 mg, 0.0764 mmol) and 2,6-dimethylphenyl isocyanide (50.0 mg, 0.381 mmol) in distilled dichloromethane (5 mL), and the resulting orange-red solution was heated at 42 °C for a period of 48 hours over which time it became yellow in colour. The solution was cooled and concentrated *in vacuo*, and chromatographed on silica gel (3% methanol in dichloromethane) furnishing crude **497** (100.3 mg) as a yellow powder which contained significant levels of unidentified impurities (including excess isocyanide starting material). No further purification of **497** was undertaken, and characterization of **497** was limited to ^{1}H NMR and GCOSY spectroscopy. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.03 (dd, 1H, J_{H4-H5} = 10.8 Hz, J_{H5-H6} = 14.0 Hz, H$_5$), 5.78 (dd, 1H, J_{H3-H4} = 15.0 Hz, J_{H4-H5} = 10.8 Hz, H$_4$), 5.66 (dq, 1H, J_{H5-H6} = 14.0 Hz, J_{H6-Me} = 6.5 Hz, H$_6$), 5.01 (dt, 1H, J_{H2-H3} = 7.8 Hz, J_{H3-H4} = 15.0 Hz, H$_3$), 2.45 (s, 12H, Ar-Me), 2.41 (s, 15H, CpMe$_5$), 2.22 (s, 6H, Ar-Me), 1.88 (d, 2H, J_{H2-H3} = 7.8 Hz, H$_2$), 1.76 (d, 3H, J_{H6-H7} = 6.5 Hz, H$_7$); ^{1}H-^{1}H GCOSY (500 MHz, CDCl$_3$) δ 6.03 ↔ δ 5.78, δ 5.66, δ 1.76; δ 5.78 ↔ δ 5.01, δ 1.88; δ 5.66 ↔ δ 1.76; δ 5.01 ↔ δ 1.88.



Probe reaction of Cp*Co(III) 1,2-dimethylpentadienyl hexafluorophosphate (453) with acetylene: A small bomb was charged with a solution of pentadienyl complex **453** (26.8 mg, 0.0617 mmol) in distilled dichloromethane (10 mL), and the resulting orange-red solution was streamed with acetylene for several minutes to ensure saturation. The bomb was sealed and heated in an oil bath at 42 °C for 16 hours. The bomb was cooled and opened, and the solvent was removed *in vacuo* furnishing an orange-red residue that was chromatographed on silica gel (3% methanol in dichloromethane). An orange-red band was eluted and, upon removal of solvent and drying under vacuum, a mixture (19.3 mg, ~ 68%) of **515** (23% of whole), **516** (16% of whole), and **517** (61% of whole) was recovered. Compound **517**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (app. td, 1H, $J_{H1\text{-}H2}$ = 7.8 Hz, $J_{H1\text{-}H7eq}$ = 9.2 Hz, $J_{H1\text{-}H7ax}$ = 3.9 Hz, H_1), 3.32 (d, 1H, $J_{H1\text{-}H2}$ = 7.8 Hz, H_2), 3.20 (app. t of d, 1H, $J_{H7ax\text{-}H7eq}$ = 15.4 Hz, $J_{H1\text{-}H7eq}$ = 9.2 Hz, $J_{H6\text{-}H7eq}$ = 7.8 Hz, H_{7eq}), 2.78 (app. t of d, 1H, $J_{H5\text{-}H6}$ = 7.2 Hz, $J_{H6\text{-}H7eq}$ = 7.8 Hz, $J_{H6\text{-}H7ax}$ = 4.5 Hz, H_6), 2.40 (m, 1H, H$_4$), 2.27 (m, 1H, H$_5$), 2.13 (dm, 1H, $J_{H7ax\text{-}H7eq}$ = 15.4 Hz, H$_{7ax}$), 1.89 (s, 3H, C$_3$-CH$_3$), 1.79 (s, 15H, CpMe$_5$), 1.40 (d, 3H, $J_{H4\text{-}CH3}$ = 7.0 Hz, C$_4$-CH$_3$); ^{1}H-^{1}H GCOSY (400 MHz, CDCl$_3$) δ 3.88 ↔ δ 3.32, δ 3.20, δ 2.13; δ 3.32 ↔ δ 1.89; δ 3.20 ↔ δ 2.78, δ 2.27, δ 2.13; δ 2.78 ↔ δ 2.27, δ 2.13; δ 2.40 ↔ δ 2.27, δ 1.40. Compound **515**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.73 (d, 1H, $J_{H3\text{-}H4}$ = 7.1 Hz, H$_3$), 6.08 (q, 1H, $J_{H9\text{-}Me}$ = 7.4 Hz, H$_9$), 5.24 (app. t of d, 1H, $J_{H3\text{-}H4}$ = 7.1 Hz, $J_{H4\text{-}H5}$ = 8.8 Hz, $J_{H(1\text{ or }6)\text{-}H4}$ = 1.2 Hz, H$_4$), 4.64 (dt, 1H, $J_{H4\text{-}H5}$ = 8.8 Hz, $J_{H5\text{-}H6a}$ = $J_{H5\text{-}H6b}$ = 4.4 Hz, H$_5$), 4.22 (dd, 1H, $J_{H1\text{-}H7(a\text{ or }b)}$ = 9.7 Hz, $J_{H1\text{-}H7(a\text{ or }b)}$ = 4.0 Hz, H$_1$), 2.52 (m, 1H, H$_{6a}$), 2.04 (s, 3H, C$_8$-C$\underline{H}_3$), 2.01 (m, 1H, H$_{7a}$), 1.88 (d, 3H, $J_{H9\text{-}Me}$ = 7.4 Hz, C$_9$-C$\underline{H}_3$), 1.79 (s, 15H, CpMe$_5$), 1.60 (m, 1H, H$_{6b}$), 0.61 (m, 1H, H$_{7b}$); ^{1}H-^{1}H GCOSY (400 MHz, CDCl$_3$) δ 6.73 ↔ δ 5.24, δ 4.22; δ 6.08 ↔ δ 1.88; δ 5.24 ↔ δ 4.64; δ 4.64 ↔ δ 2.52; δ 4.22 ↔ δ 2.52, δ 2.01, δ 0.61; δ 2.52 ↔ δ 2.01, δ 1.60, δ 0.61; δ 2.01 ↔ δ 0.61; δ 1.60 ↔ δ 0.61. Compound **516**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.67 (ddd, 1H, $J_{H3\text{-}H4}$ = 7.3 Hz, $J_{H2\text{-}H3}$ = 5.7 Hz, $J_{H(1\text{ or }5)\text{-}H3}$ = 1.1 Hz, H$_3$), 5.34 (dd, 1H, $J_{H2\text{-}H3}$ = 5.7 Hz, $J_{H1\text{-}H2}$ = 8.2 Hz, H$_2$), 4.85 (dd, 1H, $J_{H3\text{-}H4}$ = 7.3 Hz, $J_{H4\text{-}H5}$ = 9.2 Hz, H$_4$), 4.24 (m, 1H, H$_5$), 3.84 (ddd, 1H, $J_{H1\text{-}H2}$ = 8.2 Hz , $J_{H1\text{-}H7}$ = 4.3 Hz, $J_{H1\text{-}H(3\text{ or }6)}$ = 1.9 Hz, H$_1$), 2.54 (m, 1H, H$_6$), 1.79 (s, 15H, CpMe$_5$), 0.99 (d, 3H, $J_{H7\text{-}CH3}$ = 6.8 Hz, C$_7$-C$\underline{H}_3$), 0.85 (d, 3H, $J_{H6\text{-}CH3}$ = 6.7 Hz, C$_6$-C$\underline{H}_3$), 0.07 (m, 1H, H$_7$); ^{1}H-^{1}H GCOSY (400 MHz, CDCl$_3$) δ 6.67 ↔ δ 5.34, δ 4.85; δ 5.34 ↔ δ 3.84; δ 4.85 ↔ δ 4.24; δ 4.24 ↔ δ 2.54; δ 3.84 ↔ δ 0.07; δ 2.54 ↔ δ 0.07.

Notes and References

1. Hanson, J. R. *Nat. Prod. Rep.* **2000**, *17*, 165-174.
2. Hanson, J. R. *Nat. Prod. Rep.* **2001**, *18*, 88-94.
3. Hanson, J. R. *Nat. Prod. Rep.* **2002**, *19*, 125-132.
4. Hanson, J. R. *Nat. Prod. Rep.* **2003**, *20*, 70-78.
5. Hanson, J. R. *Nat. Prod. Rep.* **2004**, *21*, 785-793.
6. Hanson, J. R. *Nat. Prod. Rep.* **2005**, *22*, 594-602.
7. Hanson, J. R. *Nat. Prod. Rep.* **2006**, *23*, 875-885.
8. Fraga, B. M. *Nat. Prod. Rep.* **2000**, *17*, 483-504.
9. Fraga, B. N. *Nat. Prod. Rep.* **2001**, *18*, 650-673.
10. Fraga, B. M. *Nat. Prod. Rep.* **2002**, *19*, 650-672.
11. Fraga, B. M. *Nat. Prod. Rep.* **2003**, *20*, 392-413.
12. Fraga, B. M. *Nat. Prod. Rep.* **2004**, *21*, 669-693.
13. Fraga, B. M. *Nat. Prod. Rep.* **2005**, *22*, 465-486.
14. Fraga, B. M. *Nat. Prod. Rep.* **2006**, *23*, 943-972.
15. Yet, L. *Chem. Rev.* **2000**, *100*, 2963-3007.
16. Battiste, M. A.; Pelphrey, P. M.; Wrightthl, D. L. *Chem. Eur. J.* **2006**, *12*, 3438-3447.
17. Dzwiniel, T. L. *Cobalt-Mediated Allyl/Alkyne Cycloadditions*, Ph. D., University of Alberta, **1999**.
18. Link, J. T. *Org. React.* **2002**, *60*, 157-534.
19. Link, J. T.; Overman, L. E. *Chemtech* **1988**, *28*, 19-26.

20. Overman, L. E.; Link, J. T. In *Cross Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; VCH: Weinheim, 1998, p 231-269.

21. Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945-2964.

22. Sato, Y.; Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 1624-1634.

23. Sato, Y.; Takimoto, M.; Mori, M. *J. Synth. Org. Chem Jpn.* **2001**, *59*, 576-588.

24. Sato, Y.; Takanashi, T.; Hoshiba, M.; Mori, M. *J. Organomet. Chem.* **2003**, *688*, 36-48.

25. Makino, T.; Itoh, K. *Tetrahedron Lett.* **2003**, *44*, 6335-6338.

26. Makino, T.; Itoh, K. *J. Org. Chem.* **2004**, *69*, 395-405.

27. Matsuda, T.; Makino, M.; Murakami, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4608-4611.

28. Lu, Y. F.; Green, J. R. *Synlett* **2001**, 243-247.

29. Green, J. C. *Synlett* **2001**, 353-356.

30. Graening, T.; Bette, V.; Neudorfl, J.; Lex, J.; Schmalz, H. G. *Org. Lett.* **2005**, *7*, 4317-4320.

31. Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720-1.

32. Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940-1941.

33. Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164-4165.

34. Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A.; Pleuss, N. *Tetrahedron* **1998**, *54*, 7203-7220.

35. Wender, P. A.; Rieck, H.; Fuji, M. *J. Am. Chem. Soc.* **1998**, *120*, 10976-10977.

36. Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348-5349.

37. Wender, P. A.; Fuji, M.; Husfeld, C. O.; Love, J. A. *Org. Lett.* **1999**, *1*, 137-139.

38. Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442-10443.

39. Wender, P. A.; Dyckman, A. J. *Org. Lett.* **1999**, *1*, 2089-2092.

40. Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Scanio, M. J. C. *Org. Lett.* **2000**, *2*, 1609-1611.

41. Wender, P. A.; Barzilay, C. M.; Dyckman, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 179-180.

42. Wender, P. A.; Gamber, G. G.; Scanio, M. J. C. *Angew. Chem. Int. Ed.* **2001**, *40*, 3895-3897.

43. Wender, P. A.; Bi, F. C.; Gamber, G. G.; Gosselin, F.; Hubbard, R. D.; Scanio, M. J. C.; Sun, R.; Williams, T. J.; Zhang, L. *Pure Appl. Chem.* **2002**, *74*, 25-31.

44. Wender, P. A.; Williams, T. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4550-4553.

45. Wender, P. A.; Pedersen, T. M.; Scanio, M. J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15154-15155.

46. Yu, Z. X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 9154-9155.

47. Wegner, H. A.; de Meijere, A.; Wender, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 6530-6531.

48. Trost, B. M.; Shen, H. C.; Horne, D. B.; Toste, F. D.; Steinmetz, B. G.; Koradin, C. *Chem. Eur. J.* **2005**, *11*, 2577-2590.

49. Trost, B. M.; Shen, H. C.; Schulz, T.; Koradin, C.; Schirok, H. *Org. Lett.* **2003**, *5*, 4149-4151.

50. Barry M. Trost, H. C. S. *Angew. Chem. Int. Ed.* **2001**, *40*, 2313-2316.

51. Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc.* **2000**, *122*, 2379-2380.

52. Trost, B. M.; Shen, H. C. *Org. Lett.* **2000**, *2*, 2523-2525.

53. Barluenga, J.; Alonso, J.; Fananas, F. J.; Borge, J.; Garcia-Granda, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 5510-5513.

54. Tanino, K.; Kondo, F.; Shimizu, T.; Miyashita, M. *Org. Lett.* **2002**, *4*, 2217-2219.

55. Tanino, K.; Shimizu, T.; Miyama, M.; Kuwajima, I. *J. Am. Chem. Soc.* **2000**, *122*, 6116-6117.

56. Rumbo, A.; Castedo, L.; Mourino, A.; Mascarenas, J. L. *J. Org. Chem.* **1993**, *58*, 5585-5586.

57. Mascarenas, J. L.; Perez, I.; Rumbo, A.; Castedo, L. *Synlett* **1997**, 81-82.

58. Mascarenas, J. L.; Rumbo, A.; Castedo, L. *J. Org. Chem.* **1997**, *62*, 8620-8621.

59. Rumbo, A.; Castedo, L.; Mascarenas, J. L. *Tetrahedron Lett.* **1997**, *38*, 5885-5886.

60. Rodriguez, J. R.; Rumbo, A.; Castedo, L.; Mascarenas, J. L. *J. Org. Chem.* **1999**, *64*, 4560-4563.

61. Rodriguez, J. R.; Rumbo, A.; Castedo, L.; Mascarenas, J. L. *J. Org. Chem.* **1999**, *64*, 966-970.

62. Lopez, F.; Castedo, L.; Mascarenas, J. L. *Org. Lett.* **2000**, *2*, 1005-1007.

63. Lopez, F.; Castedo, L.; Mascarenas, J. L. *Org. Lett.* **2001**, *3*, 623-625.

64. Delgado, A.; Castedo, L.; Mascarenas, J. L. *Org. Lett.* **2002**, *4*, 3091-3094.

65. Lopez, F.; Castedo, L.; Mascarenas, J. L. *Org. Lett.* **2002**, *4*, 3683-3685.

66. Lopez, F.; Castedo, L.; Mascarenas, J. L. *Chem. Eur. J.* **2002**, *8*, 884-899.

67. Lopez, F.; Castedo, L.; Mascarenas, J. L. *J. Org. Chem.* **2003**, *68*, 9780-9786.

68. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1-19.

69. Mann, J. *Tetrahedron* **1986**, *42*, 4611-4659.

70. Harmata, M. *Tetrahedron* **1997**, *53*, 6235-6280.

71. Rigby, J. H.; Pigge, F. C. *Org. React.* **1997**, *51*, 351.

72. Sasaki, T.; Ishibashi, Y.; Ohno, M. *Tetrahedron Lett.* **1982**, *23*, 1693-1696.

73. Blackburn, C.; Childs, R. F.; Kennedy, R. A. *Can. J. Chem.* **1983**, *61*, 1981-1986.

74. Harmata, M.; Sharma, U. *Org. Lett.* **2000**, *2*, 2703-2705.

75. Funk, R.; Aungst, R. *Org. Lett.* **2001**, *3*, 3553-3555.

76. Saez, J. A.; Arno, M.; Domingo, L. R. *Org. Lett.* **2003**, *5*, 4117-4120.

77. Saez, J. A.; Arno, M.; Domingo, L. R. *Tetrahedron* **2005**, *61*, 7538-7545.

78. Davies, H. M. L.; Dai, X. *J. Am. Chem. Soc.* **2004**, *126*, 2692-2693.

79. Barluenga, J.; Alonso, J.; Rodríguez, F.; Fañanás, F. J. *Angew. Chem. Int. Ed.* **2000**, *39*, 2459-2462.

80. Saito, S.; Takeuchi, K. *Tetrahedron Lett.* **2007**, *48*, 595-598.

81. Ni, Y. K.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 11162-11163.

82. Ni, Y.; Montgomery, J. *J. Am. Chem. Soc.* **2006**, *128*, 2609-2614.

83. Bennacer, B.; Fujiwara, M.; Lee, S. Y.; Ojima, I. *J. Am. Chem. Soc.* **2005**, *127*, 17756-17767.

84. Barluenga, J.; Barrio, P.; Lopez, L. A.; Tomas, M.; Garcia-Granda, S.; Alvarez-Rua, C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3008-3011.

85. Barluenga, J.; Vicente, R.; Barrio, P.; Lopez, L. A.; Tomas, M.; Borge, J. *J. Am. Chem. Soc.* **2004**, *126*, 14354-14355.

86. Komagawa, S.; Saito, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 2446-2449.

87. Maeda, K.; Saito, S. *Tetrahedron Lett.* **2007**, *48*, 3173-3176.

88. Zora, M.; Acikgoz, C.; Odabasoglu, M.; Buyukgungor, O. *J. Organomet. Chem.* **2007**, *692*, 1571-1578.

89. Wender, P. A.; Deschamps, N. M.; Gamber, G. G. *Angew. Chem. Int. Ed.* **2003**, *42*, 1853-1857.

90. Lutsenko, Z. L.; Petrovskii, P. V.; Bezrukova, A. A.; Rubezhov, A. Z. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 855.

91. Lutsenko, Z. L.; Petrovskii, P. V.; Bezrukova, A. A.; Rubezhov, A. Z. *Bull. Acad. Sci. USSR* **1988**, 735.

92. Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275-6.

93. Schwiebert, K. E. *New transition metal-mediated annulation processes. Seven membered carbocycles via [3+2+2] cycloaddition reactions and cyclopentene synthesis via oxidatively induced migratory insertion into an iridacyclobutane complex*, Ph. D., Indiana University, **1993**.

94. Etkin, N.; Stryker, J. M., Unpublished Work

95. Etkin, N.; Dzwiniel, T. L.; Schweibert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 9702-9703.

96. Krivykh, V. V.; Gusev, O. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR* **1984**, *33*, 1081-1083.

97. Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129-145.

98. Rosan, A. M. *J. Chem. Soc., Chem. Commun.* **1981**, 311.

99. Rosan, A. M.; Romano, D. M. *Organometallics* **1990**, *9*, 1048.

100. Ito, T.; Yoden, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2365.

101. Dzwiniel, T. L.; Etkin, N.; Stryker, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 10640-10641.

102. Stryker, J. M.; Dzwiniel, T. L.; Etkin, N.; Older, C. M. *Abstracts of Papers of the American Chemical Society* **2000**, *220*, U35-U36.

103. Dzwiniel, T. L.; Stryker, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 9184-9185.

104. Older, C. M.; Stryker, J. M. *Organometallics* **2000**, *19*, 2661-2663.

105. Dzwiniel, T. L. *Seven-membered carbocycle synthesis by cobalt-mediated [3 + 2 + 2] allyl/alkyne cycloaddition reactions and novel [5 + 2] cyclopentadiene/alkyne ring expansions*, Ph. D., University of Alberta, **1999**.

106. Chan, B. C.; Stryker, J. M., Unpublished Work

107. Pearson, A. J. *Pure Appl. Chem.* **1983**, *55*, 1767-1780.

108. Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525-543.

109. Pearson, A. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 663.

110. Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol. 12, p 637.

111. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047-3077.

112. Kane-Maguire, L. A. P.; Mouncher, P. A.; Salzer, A. *J. Organomet. Chem.* **1979**, *168*, C42-C44.

113. Kane-Maguire, L. A. P.; Mouncher, P. A.; Salzer, A. *J. Organomet. Chem.* **1988**, *347*, 383-390.

114. Wieser, M.; Karaghiosoff, K.; Beck, W. *Chem. Ber.* **1993**, *126*, 1081-1089.

115. Huffer, S.; Wieser, M.; Polborn, K.; Sunkel, K.; Beck, W. *Chem. Ber.* **1994**, *127*, 1369-1377.

116. Endeshaw, M., Unpublished Work

117. Deslongchamps, P.; Brillon, D. *Can. J. Chem.* **1987**, *65*, 43-55.

118. Connon, S. J.; Blechert, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 1900-1923.

119. Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58-71.

120. O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Miura, K.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 1091-1094.

121. O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Grubbs, R. H. *Tetrahedron Lett.* **1998**, *39*, 7427-7430.

122. Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783-3784.

123. Ma, S.; Xu, B.; Ni, B. *J. Org. Chem.* **2000**, *65*, 8532-8543.

124. Yeh, R. L.; Jiaang, W. T.; Tsai, Y. M. *J. Chin. Chem. Soc.* **1997**, *44*, 253-260.

125. Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226-2227.

126. Lenges, C. P.; Brookhart, M.; Grant, B. E. *J. Organomet. Chem.* **1997**, *528*, 199-203.

127. Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965-6979.

128. Lenges, C. P.; White, P. S.; Marshall, W. J.; Brookhart, M. *Organometallics* **2000**, *19*, 1247-1254.

129. Alder, R. W.; East, S. P. *Chem. Rev.* **1996**, *96*, 2097-2112.

130. Winkler, J.; Rouse, M.; Greaney, M.; Harrison, S.; Jeon, Y. *J. Am. Chem. Soc.* **2002**, *124*, 9726-9728.

131. Kigoshi, H.; Suzuki, Y.; Aoki, K.; Uemura, D. *Tetrahedron Lett.* **2000**, *41*, 3927-3930.

132. Watanabe, K.; Suzuki, Y.; Aoki, K.; Sakakura, A.; Suenaga, K.; Kigoshi, H. *J. Org. Chem.* **2004**, *69*, 7802-7808.

133. Tang, H. F.; Yusuff, N.; Wood, J. L. *Org. Lett.* **2001**, *3*, 1563-1566.

134. Nickel, A.; Maruyama, T.; Tang, H.; Murphy, P. D.; Greene, B.; Yusuff, N.; Wood, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 16300-16301.

135. Nakamura, T.; Matsui, T.; Tanino, K.; Kuwajima, I. *J. Org. Chem.* **1997**, *62*, 3032-3033.

136. Tanino, K.; Onuki, K.; Asano, K.; Miyashita, M.; Nakamura, T.; Takahashi, Y.; Kuwajima, I. *J. Am. Chem. Soc.* **2003**, *125*, 1498-1500.

137. Kuwajima, I.; Tanino, K. *Chem. Rev.* **2005**, *105*, 4661-4670.

138. Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791-799.

139. Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8-23.

140. Honeycutt, S. C. *J. Organomet. Chem.* **1971**, *29*, 1-5.

141. Maercker, A.; Theysohn, W. *Liebigs Ann. Chem.* **1971**, *747*, 70-83.

142. Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560-562.

143. Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972-989.

144. Tolman, C. A.; Seidel, W. C.; Druliner, J. D.; Domaille, P. J. *Organometallics* **1984**, *3*, 33-38.

145. Brunkan, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627-3641.

146. Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649-52.

147. Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1987**, 2103-6.

148. Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1988**, 473-6.

149. Itoh, K.; Nakanishi, S.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2965-77.

150. Corey, E. J.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1967**, *89*, 2755.

151. Hegedus, L. S.; Stiverson, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 3250.

152. Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593.

153. Miller, L. L.; Hegedus, L. S. *J. Am. Chem. Soc.* **1975**, *97*, 459.

154. Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

155. Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172-7.

156. Grisso, B. A.; Johnson, J. R.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 5160-5.

157. Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4201-4210.

158. Ogoshi, S.; Tomiyasu, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 11598-11599.

159. Ogoshi, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 9020-9021.

160. Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel, Vol. 1: Organonickel Complexes*, 1974.

161. Van der Linde, R.; Bogdanovic, B. 1969.

162. Norman, D. W.; Ferguson, M. J.; McDonald, R.; Stryker, J. M. *Organometallics* **2006**, *25*, 2705-2708.

163. Norman, D. W. *Synthesis and Reactivity of New Thermally Stable Chromium(II)/(III) eta^3-Allyl and s-Trans Chromium Diene Complexes*, Ph. D., University of Alberta, **2006**.

164. Howell, J. A. S.; Dixon, D. T.; Kola, J. C. *J. Organomet. Chem.* **1984**, *266*, 69-82.

165. Kanaya, S.; Imai, Y.; Komine, N.; Hirano, M.; Komiya, S. *Organometallics* **2005**, *24*, 1059-1061.

166. Torraca, K. E.; McElwee-White, L. *Coord. Chem. Rev.* **2000**, *206*, 469-491.

167. Astruc, D. *Chem. Rev.* **1988**, *88*, 1189-1216.

168. Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. *Organometallics* **1986**, *5*, 1352-1359.

169. Hine, K. E.; Childs, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 3289-3294.

170. Ikuno, K.; Kobayashi, T.; Harada, T.; Noguchi, M.; Kakehi, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1445-1452.

171. Ernst, R. D. *Comments Inorg. Chem.* **1999**, *21*, 285-325.

172. Bennett, M. A.; Nicholls, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328-1330.

173. Wooster, T. T.; Geiger, W. E.; Ernst, R. D. *Organometallics* **1995**, *14*, 3455-3460.

174. Bleeke, J. R.; Peng, W.-J. *Organometallics* **1986**, *5*, 635-644.

175. Arif, A. M.; Ernst, R. D.; Melendez, E.; Rheingold, A. L.; Waldman, T. E. *Organometallics* **1995**, *14*, 1761-1769.

176. Bleeke, J. R.; Earl, P. L. *Organometallics* **1989**, *8*, 2735-2737.

177. Hyla-Kryspin, I.; Waldman, T. E.; Melendez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030-5040.

178. Varga, V.; Polasek, N.; Hiller, J.; Thewalt, U.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 1268-1274.

179. Ishii, Y.; Gao, C.; Iwasaki, M.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 695-696.

180. Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 8296-8297.

181. Kralik, M. S.; Rheingold, A. L.; Hutchinson, J. P.; Freeman, J. W.; Ernst, R. D. *Organometallics* **1996**, *15*, 551-561.

182. Kreiter, C. G.; Lehr, K.; Leyendecker, M.; Sheldrick, W. S.; Exner, R. *Chem. Ber.* **1991**, *124*, 3-12.

183. Kreiter, C. G.; Lehr, K. *J. Organomet. Chem.* **1991**, *406*, 159-170.

184. Kreiter, C. G.; Lehr, K.; Heeb, G. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 941-949.

185. Kreiter, C. G.; Lehr, K. *J. Organomet. Chem.* **1993**, *448*, 107-117.

186. Kreiter, C. G.; Koch, E. C.; Frank, W.; Reiss, G. *Inorg. Chim. Acta* **1994**, *220*, 77-83.

187. Kreiter, C. G.; Koch, E. C.; Frank, W.; Reiss, G. J. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1473-1485.

188. Kreiter, C. G.; Fiedler, C.; Frank, W.; Reiss, G. J. *Chem. Ber.* **1995**, *128*, 515-518.

189. Kreiter, C. G.; Koch, E. C.; Frank, W.; Reiss, G. J. *J. Organomet. Chem.* **1995**, *490*, 125-131.

190. Kreiter, C. G.; Fiedler, C.; Frank, W.; Reiss, G. J. *J. Organomet. Chem.* **1995**, *490*, 133-141.

191. Wang, C.; Sheridan, J. B.; Chung, H. J.; Cote, M. L.; Lalancette, R. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8966-8972.

192. Chen, W. C.; Chung, H. J.; Wang, C. J.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 3337-3344.

193. Chung, H.-J.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 4575-4585.

194. Wilson, A. M.; Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 6252-6254.

195. Tomaszewski, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; Gleiter, R.; Ernst, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 2959-2960.

196. Harvey, B. G.; Mayne, C. L.; Arif, A. M.; Tomaszewski, R.; Ernst, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 16426-16435.

197. Basta, R.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2004**, *357*, 3883-3888.

198. Yueh, T.-C.; Lush, S.-F.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1996**, *15*, 5669-5673.

199. Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634-2643.

200. Cracknell, R. B.; Nicholls, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446-448.

201. Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781-1787.

202. Slegeir, W.; Case, R.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 287-288.

203. Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15-17.

204. Older, C. M.; McDonald, R.; Stryker, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 14202-14203.

205. Older, C. M. *Allyl/Alkyne Coupling Reactions Mediated by Ruthenium(II): Carbon-Carbon Bond Activations and Multicomponent Cycloadditions*, University of Alberta, **2000**.

206. Chan, B. C.; Stryker, J. M., Unpublished Work

207. Nakamura, E.; Ammal, S. C.; Stryker, J. M., Unpublished Work

208. Alvarez, P.; Gimeno, J.; Lastra, E. *Organometallics* **2002**, *21*, 5678-5680.

209. Alvarez, P.; Gimeno, J.; Lastra, E.; Garcia-Granda, S.; Van der Maelen, J. F.; Bassetti, M. *Organometallics* **2001**, *20*, 3762-3771.

210. Fryzuk, M. D.; Petrella, M. J.; Patrick, B. O. *Organometallics* **2005**, *24*, 5440-5454.

211. Fryzuk, M. D.; Petrella, M. J.; Coffin, R. C.; Patrick, B. O. *C. R. Chim.* **2002**, *5*, 451-460.

212. Ashworth, T. V.; Nolte, M. J.; Reimann, R. H.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1977**, 937-939.

213. Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 1102-1104.

214. Lange, G.; Reimelt, O.; Jessen, L.; Heck, J. *Eur. J. Inorg. Chem.* **2000**, 1941-1952.

215. Connelly, N. G.; Gilbert, M.; Orpen, A. G.; Sheridan, J. B. *J. Chem. Soc., Dalton Trans.* **1990**, 1291-1300.

216. Bennett, M. A.; Willis, A. C. *Polyhedron* **1996**, *15*, 3559-3567.

217. Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1981**, *20*, 2353-2365.

218. Wiles, J. A.; Lee, C. E.; McDonald, R.; Bergens, S. H. *Organometallics* **1996**, *15*, 3782-3784.

219. McComas, C. C.; Ziller, J. W.; Van Vranken, D. L. *Organometallics* **2000**, *19*, 2853-2857.

220. Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1988**, 951-953.

221. Hetterscheid, D. G. H.; de Bruin, B.; Smits, J. M. M.; Gal, A. W. *Organometallics* **2003**, *22*, 3022-3024.

222. Evans, J.; Johnson, B. F. G.; Lewis, J. *Chem. Commun.* **1971**, 1252-1253.

223. Burrows, A. D.; Green, M.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. *Angew. Chem. Int. Ed.* **1999**, *38*, 3043-3045.

224. Oshima, N.; Hamatani, Y.; Fukui, H.; Suzuki, H.; Morooka, Y. *J. Organomet. Chem.* **1986**, *303*, C21-C24.

225. Hodson, B. E.; Ellis, D.; McGrath, T. D.; Monaghan, J. J.; Rosair, G. M.; Welch, A. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 715-717.

226. Jeffery, J. C.; Stone, G. A.; Topaloglu, I. *Polyhedron* **1993**, *12*, 319-325.

227. White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305-1311.

228. Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1972**, 2668-2675.

229. Dorta, R.; Togni, A. *Organometallics* **1998**, *17*, 5441-5444.

230. Bushnell, G. W.; Fjeldsted, D. O. K.; Stobart, S. R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 580-581.

231. Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* **1977**, *125*, 303-312.

232. Martin, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406-5417.

233. Angermund, K. P.; Betz, P.; Butenschon, H. *Chem. Ber.* **1993**, *126*, 713-724.

234. Spencer, D. M.; Beddoes, R. L.; Helliwell, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **2003**, 638-650.

235. Beddoes, R. L.; Spencer, D. M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2915-2917.

236. Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409-1411.

237. Carruthers, K. P.; Helliwell, M.; Hinchliffe, J. R.; de Souza, A.-L. A. B.; Spencer, D. M.; Whiteley, M. W. *J. Organomet. Chem.* **2004**, *689*, 848-859.

238. Basta, R.; Arif, A. M.; Ernst, R. D. *J. Organomet. Chem.* **2004**, *689*, 685-688.

239. Margulis, T. N.; Schiff, L.; Rosenblum, M. *J. Am. Chem. Soc.* **1965**, *87*, 3269-3270.

240. Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 145-149.

241. Johnson, B. F. G.; Lewis, J.; Randall, G. L. P. *J. Chem. Soc.* **1971**, 422-429.

242. Charles, A. D.; Diversi, P.; Johnson, B. F. G.; Karlin, K. D.; Lewis, J.; Rivera, A. V.; Sheldrick, G. M. *J. Organomet. Chem.* **1977**, *128*, C31-C34.

243. Rivera, A. V.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Sci.* **1978**, *B34*, 1716-1718.

244. Charles, A. D.; Diversi, P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1906-1917.

245. Hueffer, S.; Wieser, M.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1994**, *481*, 45-55.

246. Eisenstadt, A.; Winstein, S. *Tetrahedron Lett.* **1970**, 4603-4606.

247. Eisenstadt, A. *J. Organomet. Chem.* **1972**, *38*, C32-C34.

248. Bluemel, J.; Hertkorn, N.; Kanellakopulos, B.; Koehler, F. H.; Lachmann, J.; Mueller, G.; Wagner, F. E. *Organometallics* **1993**, *12*, 3896-3905.

249. Lewis, J.; Parkins, A. W. *J. Chem. Soc. A* **1969**, 953-957.

250. Lustgarten, R. K.; Brookhart, M.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6350-6352.

251. Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 497-498.

252. McFarlane, L.; Pratt, L.; Wilkinson, G. *J. Chem. Soc. A* **1963**, 2162-2166.

253. Salzer, A.; Bigler, P. *Inorg. Chim. Acta* **1981**, *48*, 199-203.

254. Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401-2405.

255. Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588-1596.

256. Bleeke, J. R.; Peng, W. J. *Organometallics* **1987**, *6*, 1576-1578.

257. Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W.; Haile, T.; Beatty, A. M.; Xie, Y. F. *Organometallics* **1991**, *10*, 2391-2398.

258. Bleeke, J. R.; Rohde, A. M.; Boorsma, D. W. *Organometallics* **1993**, *12*, 970-974.

259. Bleeke, J. R.; Luaders, S. T. *Organometallics* **1995**, *14*, 1667-1673.

260. Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367-1369.

261. Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 486-491.

262. Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Organometallics* **1988**, *7*, 1417-1425.

263. Bleeke, J. R.; Wittenbrink, R. J.; Clayton, T. W.; Chiang, M. Y. *J. Am. Chem. Soc.* **1990**, *112*, 6539-6545.

264. Bleeke, J. R.; Wittenbrink, R. J. *J. Organomet. Chem.* **1991**, *405*, 121-132.

265. Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328-2339.

266. Bleeke, J. R.; Rauscher, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972-8973.

267. Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1985**, *4*, 194-197.

268. Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics* **1986**, *5*, 1642-1647.

269. Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417-423.

270. Bleeke, J. R.; Moore, D. A. *Inorg Chem* **1986**, *25*, 3522-3526.

271. Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Organometallics* **1987**, *6*, 2614-2617.

272. Oppolzer, W.; Snowden, R. L.; Simmons, D. P. *Helv. Chim. Acta* **1981**, *64*, 2002-2021.

273. Honda, T.; Mizutani, H.; Kanai, K. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1729-1739.

274. Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691-2694.

275. Brookhart, M.; Lincoln, D. M.; Volpe, A. F.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212-1218.

276. Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1-100.

277. Kirk, A. D., Unpublished Work

278. Kirk, A. D. *Ancillary Ligand Effects in the Cobalt-mediated [5+2] Pentadienyl/Alkyne Cycloaddition Reactions*, M.Sc., University of Alberta, **2007**.

279. Ylijoki, K. E. O., Unpublished Work

280. Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25-C27.

281. Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15.

282. Nicholls, J. C.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 278.